## Supporting Information for

# Phenothiazine Radical Cation Excited States as Super-oxidants for 

## Energy Demanding Reactions

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## 1. Materials, Synthesis, and Characterization

### 1.1 Materials

All chemicals were obtained from commercial suppliers and used as received unless otherwise noted. Column chromatography was performed using silica gel from Sorbent Technologies. 1H and 13C NMR spectra were recorded at ambient temperature at 500 MHz or 126 MHz , respectively, using a Bruker Avance III spectrometer with chemical shifts reported in ppm relative to TMS. NMR resonance multiplicities are reported with the following abbreviations: $\mathrm{s}=$ singlet, $\mathrm{d}=$ doublet, and $\mathrm{m}=$ multiplet, and coupling constants are reported in Hz. High resolution electrospray ionization (ESI) mass spectra were obtained on an Agilent 6210A LC-TOF.

### 1.2 Synthesis and Characterization

The synthesis and characterization of PTZ-Per, PTZ-BE, and PTZ-ACN are described in detail below. Molecules 3 and 4 and DPA were purchased from Sigma-Aldrich and used as received. PTZ, ${ }^{1} 1,{ }^{2} 2,{ }^{3}$ Per, ${ }^{4}$ PTZ-DPA, ${ }^{5} 5,{ }^{6}$ and $\mathrm{ACN}^{7}$ were prepared as described previously. The synthesis of PTZ-Per, PTZ-BE, and PTZ-ACN is described below.

Scheme 1. Structures of molecules examined in this study.



PTZ-Per. 10-(4-bromophenyl)-10 ${ }^{-p}$-phenothiazine ${ }^{2}(0.091 \mathrm{~g}, 0.256 \mathrm{mmol}$ ), 4,4,5,5-tetramethyl-2-(perylene-3-yl)-1,3,2-dioxaborolane ${ }^{3}(0.097 \mathrm{~g}, 0.256 \mathrm{mmol})$, and $\mathrm{Cs}_{2} \mathrm{CO}_{3}(0.82 \mathrm{~g}, 2.5 \mathrm{mmol})$ were added to THF ( 50 mL ) in a 2-neck round-bottom flask equipped with a water-jacketed reflux condenser. The solution was degassed $\left(\mathrm{N}_{2(\mathrm{~g})}\right)$ for 15 minutes. $\mathrm{Pd}\left(\mathrm{PPh}_{3}\right)_{4}(0.035 \mathrm{~g}, 0.03 \mathrm{mmol})$ was added, and the solution was stirred at reflux under $\mathrm{N}_{2(\mathrm{~g})}$ for 12 h . After cooling to room temperature, the solvent was removed by rotary evaporation, and the crude material was purified by column
chromatography on silica gel ( $25 \%$ DCM in hexanes) to give the product as a yellow powder ( $0.103 \mathrm{~g}, 76 \%$ ). ${ }^{1} \mathrm{H}$ NMR ( $500 \mathrm{MHz}, \mathrm{DMSO}-d_{6}$ ) $\delta 8.51-8.41(\mathrm{~m}, 4 \mathrm{H}), 7.89-7.83(\mathrm{~m}, 3 \mathrm{H}), 7.80$ $(\mathrm{d}, J=7.9 \mathrm{~Hz}, 2 \mathrm{H}), 7.64-7.56(\mathrm{~m}, 6 \mathrm{H}), 7.17(\mathrm{~d}, \mathrm{~J}=7.6 \mathrm{~Hz}, 1 \mathrm{H}), 7.07(\mathrm{dd}, \mathrm{J}=7.9,7.9 \mathrm{~Hz}, 1 \mathrm{H})$, $6.95(\mathrm{dd}, \mathrm{J}=7.5,7.5 \mathrm{~Hz}, 1 \mathrm{H}), 6.47(\mathrm{~d}, \mathrm{~J}=8.3 \mathrm{~Hz}, 1 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR (126 MHz, DMSO- $d_{6}$ ) $\delta$ 143.7, $143.5,141.8,135.8,133.4,132.8,130.2,129.4,129.0,128.1,127.7,127.6,125.2,123.9,121.9$, 118.4, 117.5, 105.0. HRMS (ESI) $m / z[M]^{+}$calculated for $\mathrm{C}_{38} \mathrm{H}_{23} \mathrm{NS} 525.155$, found 525.156.


PTZ-BE. 10-(4-bromophenyl)-10H-phenothiazine ${ }^{2}$ ( $1.0 \mathrm{~g}, 2.82 \mathrm{mmol}$ ) bis(pinacolato)diboron $(1.08 \mathrm{~g}, 4.23 \mathrm{mmol})$, and $\mathrm{KOAc}(0.46 \mathrm{~g}, 4.7 \mathrm{mmol})$ were added to 1,4 -dioxane $(70 \mathrm{~mL})$ in a 2 neck round-bottom flask equipped with a water-jacketed reflux condenser. The solution was degassed $\left(\mathrm{N}_{2(\mathrm{~g})}\right)$ for 15 minutes. $\mathrm{Pd}(\mathrm{dppf}) \mathrm{Cl}_{2}(0.20 \mathrm{~g}, 0.15 \mathrm{mmol})$ was added, and the solution was stirred at $75^{\circ} \mathrm{C}$ under $\mathrm{N}_{2(\mathrm{~g})}$ for 12 h . After cooling to room temperature, the solvent was removed by rotary evaporation, and the crude material was purified by column chromatography on silica gel (DCM) to give the product as a white crystalline powder $(0.91 \mathrm{~g}, 80 \%) .{ }^{1} \mathrm{H} \mathrm{NMR}(500 \mathrm{MHz}$, DMSO- $\left.d_{6}\right) \delta 7.88(\mathrm{~d}, J=8.3 \mathrm{~Hz}, 2 \mathrm{H}), 7.35(\mathrm{~d}, J=8.3 \mathrm{~Hz}, 2 \mathrm{H}), 7.18(\mathrm{dd}, J=7.5,1.6 \mathrm{~Hz}, 2 \mathrm{H})$, 7.02 (ddd, $J=7.9,7.7,1.7 \mathrm{~Hz}, 2 \mathrm{H}), 6.95(\mathrm{ddd}, J=7.5,7.5,1.3 \mathrm{~Hz}, 2 \mathrm{H}), 6.41(\mathrm{dd}, J=8.1,1.3 \mathrm{~Hz}$, 2H), 1.33 (s, 12H). ${ }^{13} \mathrm{C}$ NMR ( 126 MHz, DMSO- $d_{6}$ ) $\delta 144.5,143.4,137.3,127.9,127.6,123.9$,
122.4, 118.6, 84.3, 25.2. HRMS (ESI) $m / z[\mathrm{M}+\mathrm{H}]^{+}$calculated for $\mathrm{C}_{24} \mathrm{H}_{24} \mathrm{BNO}_{2} \mathrm{~S} 400.165$, found 400.166.


PTZ-ACN. PTZ-BE ( $0.128 \mathrm{~g}, 0.319 \mathrm{mmol}$ ), 9-bromo-10-cyanoanthracene ${ }^{6}(0.060,0.21 \mathrm{mmol})$, and $\mathrm{Cs}_{2} \mathrm{CO}_{3}(1.04 \mathrm{~g}, 3.2 \mathrm{mmol})$ were added to THF $(20 \mathrm{~mL})$ in a 2-neck round-bottom flask equipped with a water-jacketed reflux condenser. The solution was degassed $\left(\mathrm{N}_{2(\mathrm{~g})}\right)$ for 15 minutes. $\mathrm{Pd}\left(\mathrm{PPh}_{3}\right)_{4}(0.023 \mathrm{~g}, 0.02 \mathrm{mmol})$ was added, and the solution was stirred at reflux under $\mathrm{N}_{2(\mathrm{~g})}$ for 16 h . After cooling to room temperature, the solvent was removed by rotary evaporation, and the crude material was purified by column chromatography on silica gel ( $30 \% \mathrm{DCM}$ in hexanes) to give the product as an orange powder $(0.059 \mathrm{~g}, 58 \%) .{ }^{1} \mathrm{H}$ NMR ( $\left.500 \mathrm{MHz}, \mathrm{DMSO}-d_{6}\right) \delta 8.44(\mathrm{~d}$, $J=8.5 \mathrm{~Hz}, 2 \mathrm{H}), 7.93(\mathrm{dd}, J=7.6,7.6 \mathrm{~Hz}, 2 \mathrm{H}), 7.85(\mathrm{~d}, J=9.0 \mathrm{~Hz}, 2 \mathrm{H}), 7.76-7.61(\mathrm{~m}, 6 \mathrm{H}), 7.23$ (d, $J=7.5 \mathrm{~Hz}, 2 \mathrm{H}), 7.16(\mathrm{dd}, J=7.9,7.9 \mathrm{~Hz}, 2 \mathrm{H}), 7.01(\mathrm{dd}, J=7.5,7.5 \mathrm{~Hz}, 2 \mathrm{H}), 6.67(\mathrm{~d}, J=8.1$ $\mathrm{Hz}, 2 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR (126 MHz, DCM- $d_{2}$ ) 144.1, 143.0, 141.8, 136.5, 133.19, 133.17, 129.7, 129.4, $128.9,127.8,127.2,127.1,126.6,125.6,123.2,122.2,117.6,117.3,106.1$. HRMS (ESI) $\mathrm{m} / \mathrm{z}$ $[\mathrm{M}+\mathrm{H}]^{+}$calculated for $\mathrm{C}_{33} \mathrm{H}_{20} \mathrm{~N}_{2} \mathrm{~S} 476.134$, found 476.135.

## 2. Steady-State Optical Spectroscopy



Figure S1. Normalized steady-state absorption spectra of PTZ containing dyads (red) overlaid with their monomeric hole-accepting moieties (black).

## 3. Electrochemistry



Figure S2. Cyclic voltammograms of the PTZ containing dyads (solid line) compared with their monomeric hole accepting moieties.

## 4. Transient Absorption Spectroscopy

The data were globally fit either to specified kinetic models or a sum of exponentials. The dataset was then deconvoluted with the resultant populations or amplitudes to reconstruct the speciesassociated or decay-associated spectra. The kinetic data from multiple different wavelengths are fit using the global analysis described below. Each wavelength is given an initial amplitude that is representative of the spectral intensity at time $t_{0}$, and varied independently to fit the data. The time/rate constants and $t_{0}$ are shared between the various kinetic data and are varied globally across the kinetic data to fit the models described below.

For the species-associated fitting, we globally fit the dataset to a specified kinetic model (shown below each data set) and use the resultant populations to deconvolute the dataset and reconstruct species-associated spectra. The MATLAB program numerically the solves the differential equations through matrix methods, then convolutes the solutions with a Gaussian instrument response function with width w (FWHM), before employing a least-squares fitting using a Levenberg-Marquardt or Simplex method to find the parameters which result in matches to the kinetic data.

For decay-associated fitting, we globally fit the dataset to a set of pre-specified mathematical functions and use the resultant function amplitudes to deconvolute the dataset and reconstruct decay-associated spectra:

$$
\begin{equation*}
S(\lambda, t)=\sum_{n} A_{n}(\lambda, 0) \exp \left[-t / \tau_{n}\right] \tag{Eqn.S1}
\end{equation*}
$$

The MATLAB program convolutes the solutions with a Gaussian instrument response function with width w (FWHM), before employing a least-squares fitting using a Levenberg-Marquardt or Simplex method to find the parameters which result in matches to the kinetic data. Each function corresponds to a given well-defined temporal process. The raw data matrix is deconvoluted with
the resultant function amplitudes as functions of time to produce the spectra associated with each mathematical component, $A_{n}(\lambda)$.

The time constants extracted from the fits of the fsTA data and summarized in Table 2 of the main text are effective time constants ( $\tau_{\text {eff }}$ ) and may be combinations of multiple photophysical processes. The effective time constants were used to determine time constants for each individual photophysical pathway to the best of our ability (displayed in Figure 8 of the main text) using Equation S2.

$$
\begin{equation*}
\frac{1}{\tau_{e f f}}=\frac{1}{\tau_{1}}+\frac{1}{\tau_{2}}+\cdots+\frac{1}{\tau_{n}} \tag{Eqn.S2}
\end{equation*}
$$



Figure S3. $\lambda_{\mathrm{ex}}=517 \mathrm{~nm}, 1.0 \mu \mathrm{~J} /$ pulse, MeCN. (A) fsTA spectra of $\mathrm{PTZ}^{+\cdot}$. (B) Species-associated spectra obtained by global fitting. (C) Transient kinetics at selected wavelengths. (D) Populations of the transient species. (E) fsTA spectra of $\mathrm{PTZ}^{+\cdot}$ expanded to show the evolution in ESA wavelength of maximum intensity over the first 100 ps .

$$
\boldsymbol{k}=\left[\begin{array}{cc}
-\boldsymbol{k}_{A \rightarrow B} & \mathbf{0} \\
\boldsymbol{k}_{A \rightarrow B} & -\boldsymbol{k}_{B \rightarrow G S}
\end{array}\right]
$$

Initial populations: $\mathrm{A}_{0}=1$ and $\mathrm{B}_{0}=0$

Following excitation at $\lambda=517 \mathrm{~nm}, \mathrm{PTZ}^{+\bullet}$ exhibits a strong excited state absorption (ESA) at $\lambda=$ 380 nm , a ground state bleach $(\mathrm{GSB})$ at $\lambda=514 \mathrm{~nm}$, and a weak ESA at $\lambda=568 \mathrm{~nm}$. Each of these signals is apparent after a 1 ps delay. The weaker ESA undergoes a hypsochromic shift from $\lambda=568$ to 548 nm as the spectra evolve over the first 50 ps (Figure S3E). The stronger ESA concomitantly undergoes a less dramatic shift from $\lambda=380$ to 374 nm . This dynamic spectral shifting is indicative of a GS recovery mechanism composed of multiple species, and this mechanism is supported by the global fitting analysis (Figure S3). Following excitation at $\lambda=$ 900 nm , the ESA features at $\lambda=380$ and 568 nm and GSB at $\lambda=514 \mathrm{~nm}$ are again apparent after a 1 ps delay, and again the ESA features again shift to $\lambda=374$ and 548 nm as the spectra evolve over the first 50 ps (Figure S5).


Figure S4. $\lambda_{\mathrm{ex}}=517 \mathrm{~nm}, 1.0 \mu \mathrm{~J} /$ pulse, MeCN. (A) NIR fsTA spectra of $\mathrm{PTZ}^{+}$. (B) Species-associated spectra obtained by global fitting. (C) Transient kinetics at selected wavelengths. (D) Populations of the transient species.

$$
k=\left[\begin{array}{cc}
-\boldsymbol{k}_{A \rightarrow B} & 0 \\
\boldsymbol{k}_{A \rightarrow B} & -\boldsymbol{k}_{B \rightarrow G S}
\end{array}\right]
$$

Initial populations: $\mathrm{A}_{0}=1$ and $\mathrm{B}_{0}=0$


Figure S5. $\lambda_{\mathrm{ex}}=900 \mathrm{~nm}, 1.0 \mu \mathrm{~J} / \mathrm{pulse}, \mathrm{MeCN}$. (A) fsTA spectra of $\mathrm{PTZ}^{+\cdot}$. (B) Species-associated spectra obtained by global fitting. (C) Transient kinetics at selected wavelengths. (D) Populations of the transient species. (E) fsTA spectra of $\mathrm{PTZ}^{+\cdot}$ expanded to show the evolution in ESA wavelength of maximum intensity over the first 100 ps .

$$
k=\left[\begin{array}{cc}
-k_{A \rightarrow B} & 0 \\
\boldsymbol{k}_{A \rightarrow B} & -k_{B \rightarrow G S}
\end{array}\right]
$$

Initial populations: $\mathrm{A}_{0}=1$ and $\mathrm{B}_{0}=0$


Figure S6. $\lambda_{\mathrm{ex}}=900 \mathrm{~nm}, 1.0 \mu \mathrm{~J} /$ pulse, MeCN . (A) NIR fsTA spectra of $\mathrm{PTZ}^{+}$. (B) Species-associated spectra obtained by global fitting. (C) Transient kinetics at selected wavelengths. (D) Populations of the transient species.

$$
\boldsymbol{k}=\left[\begin{array}{cc}
-\boldsymbol{k}_{A \rightarrow B} & \mathbf{0} \\
\boldsymbol{k}_{A \rightarrow B} & -\boldsymbol{k}_{B \rightarrow G S}
\end{array}\right]
$$

Initial populations: $\mathrm{A}_{0}=1$ and $\mathrm{B}_{0}=0$


Figure S7. $\lambda_{\mathrm{ex}}=517 \mathrm{~nm}, 1.0 \mu \mathrm{~J} / \mathrm{pulse}, \mathrm{MeCN}$. (A) fsTA spectra of PTZ $^{+}-$-Per. (B) Species-associated spectra obtained by global fitting. (C) Transient kinetics at selected wavelengths. (D) Populations of the transient species.

$$
k=\left[\begin{array}{cc}
-k_{A \rightarrow G S} & 0 \\
0 & -k_{B \rightarrow G S}
\end{array}\right]
$$

Initial populations: $\mathrm{A}_{0}=0.86$ and $\mathrm{B}_{0}=0.14$

After a delay of 0.7 ps following excitation of $\mathrm{PTZ}^{+\bullet}$-Per with a pump pulse centered at $\lambda_{\mathrm{ex}}=517$ nm , an absorptive feature at $\lambda=565 \mathrm{~nm}$, characteristic of $\mathrm{Per}^{+\bullet}$, and Per GSB features at $\lambda=416$ and 442 nm are apparent (Figure 4A). ${ }^{8}$ These features reach maximum intensity at a pump-probe delay of 1.7 ps , after which they begin to decay. Because the $\mathrm{PTZ}^{+\cdot}$ GS NIR absorption band is significantly less intense than the GS visible absorption band (Figure 1B) the samples prepared for excitation at $\lambda_{\mathrm{ex}}=900 \mathrm{~nm}$ were more concentrated than those prepared for $\lambda_{\mathrm{ex}}=517 \mathrm{~nm}$. This
resulted in the Per GS completely absorbing the light from the probe pulse between $\lambda=405$ and 450 nm , thus no data were recorded in this region.

The GS recovery dynamics of $\mathrm{PTZ}^{+}$--Per were observed to be biexponential after excitation at $\lambda_{\mathrm{ex}}=517 \mathrm{~nm}$. This is explained by structural relaxation of neutral PTZ moiety after the initial hole transfer reaction (main text). To determine the percentage of the population that decays to the GS from each Species A and Species B, the initial populations were adjusted until the magnitude of the Per GSB was equivalent for both species (Figure S7B). It was determined that $86 \%$ of the sample decays back to the ground state through Species A, and $14 \%$ of the sample decays to the ground state through Species B. From this, the time constant for the structural relaxation of the neutral PTZ moiety was estimated to be $\sim 270 \mathrm{ps}$. Using this value, a new rate matrix was used to fit the data to a model that more accurately represents the photophysical dynamics (Figure S8). This same matrix was also used to fit the data collected after excitation at $\lambda_{\mathrm{ex}}=900 \mathrm{~nm}$ (Figure S10).


Figure S8. $\lambda_{\text {ex }}=517 \mathrm{~nm}, 1.0 \mu \mathrm{~J} /$ pulse, MeCN. (A) fsTA spectra of $\mathrm{PTZ}^{+\bullet}$-Per. (B) Species-associated spectra obtained by global fitting. (C) Transient kinetics at selected wavelengths. (D) Populations of the transient species.

$$
k=\left[\begin{array}{cc}
-k_{A \rightarrow G S}-\left(\frac{1}{270}\right) & 0 \\
\left(\frac{1}{270}\right) & -k_{B \rightarrow G S}
\end{array}\right]
$$

Initial populations: $\mathrm{A}_{0}=1$ and $\mathrm{B}_{0}=0$


Figure S9. $\lambda_{\mathrm{ex}}=900 \mathrm{~nm}, 1.0 \mu \mathrm{~J} /$ pulse, MeCN. (A) fsTA spectra of $\mathrm{PTZ}^{+\bullet}$-Per. (B) Species-associated spectra obtained by global fitting. (C) Transient kinetics at selected wavelengths. (D) Populations of the transient species.

$$
k=\left[\begin{array}{cc}
-k_{A \rightarrow G S} & 0 \\
0 & -k_{B \rightarrow G S}
\end{array}\right]
$$

Initial populations: $\mathrm{A}_{0}=0.86$ and $\mathrm{B}_{0}=0.14$


Figure S10. $\lambda_{\mathrm{ex}}=900 \mathrm{~nm}, 1.0 \mu \mathrm{~J} /$ pulse, MeCN . (A) fsTA spectra of $\mathrm{PTZ}^{+\cdot}$-Per. (B) Species-associated spectra obtained by global fitting. (C) Transient kinetics at selected wavelengths. (D) Populations of the transient species.

$$
k=\left[\begin{array}{cc}
-k_{A \rightarrow G S}-\left(\frac{1}{270}\right) & 0 \\
\left(\frac{1}{270}\right) & -k_{B \rightarrow G S}
\end{array}\right]
$$

Initial populations: $\mathrm{A}_{0}=1$ and $\mathrm{B}_{0}=0$


Figure S11. $\lambda_{\mathrm{ex}}=517 \mathrm{~nm}, 1.0 \mu \mathrm{~J} /$ pulse, MeCN. (A) fsTA spectra of PTZ ${ }^{+}$-DPA. (B) Decay-associated spectra obtained by global fitting. (C) Transient kinetics at selected wavelengths. (D) Amplitudes of the exponential functions used in the fitting.

$$
\begin{aligned}
& A(t)=A_{0} \exp \left[-\frac{t}{t_{1}}\right] \\
& B(t)=B_{0} \exp \left[-\frac{t}{t_{2}}\right] \\
& C(t)=C_{0} \exp \left[-\frac{t}{t_{13}}\right]
\end{aligned}
$$

After a delay of 0.5 ps following excitation of $\mathrm{PTZ}^{+\cdot}-\mathrm{DPA}$ at $\lambda_{\mathrm{ex}}=517 \mathrm{~nm}$, features at $\lambda=417$, 589 , and 654 nm characteristic of $\mathrm{DPA}^{+\bullet}$ are apparent (Figures 5A and S11A). ${ }^{9-10}$ At delays longer than 2 ps , an absorptive feature is apparent at $\lambda=548 \mathrm{~nm}$. The decay-associated spectrum with the
shortest time constant (component A in Figures 5B and S11B) has features characteristic of the $\mathrm{PTZ}^{+\bullet} \mathrm{GSB}$ and decays with $\tau_{\mathrm{A}}=0.9 \pm 0.3 \mathrm{ps}$. Component B in Figure 5B has features at $\lambda=417$, 589 , and 654 nm , characteristic of $\mathrm{DPA}^{+\cdot}$, and this component decays with a time constant of $\tau_{\mathrm{B}}=$ $4.1 \pm 0.3 \mathrm{ps}$. Component C is the decay of the feature at $\lambda=548 \mathrm{~nm}$, and it decays with a time constant of $\tau_{\mathrm{C}}=20 \pm 2 \mathrm{ps}$. Following excitation at $\lambda_{\mathrm{ex}}=900 \mathrm{~nm}$ features assigned to $\mathrm{DPA}^{+\cdot}$ and the $\mathrm{PTZ}^{+\cdot} \mathrm{GSB}$ are again apparent after a delay of 0.5 ps . Unlike the spectra following $\lambda_{\mathrm{ex}}=517$ nm excitation, when the sample is excited at $\lambda_{\mathrm{ex}}=900 \mathrm{~nm}$ the feature at $\lambda=548 \mathrm{~nm}$ is not significant at longer time delays (Figures 5C and S12A).


Figure S12. $\lambda_{\text {ex }}=900 \mathrm{~nm}, 1.0 \mu \mathrm{~J} /$ pulse, MeCN. (A) fsTA spectra of PTZ ${ }^{+}$-DPA. (B) Decay-associated spectra obtained by global fitting. (C) Transient kinetics at selected wavelengths. (D) Amplitudes of the exponential functions used in the fitting.

$$
\begin{aligned}
& A(t)=A_{0} \exp \left[-\frac{t}{t_{1}}\right] \\
& B(t)=B_{0} \exp \left[-\frac{t}{t_{2}}\right]
\end{aligned}
$$



Figure S13. (A) NIR probe fsTA spectra of $\mathrm{PTZ}^{+\bullet}$-DPA $\lambda_{\mathrm{ex}}=517 \mathrm{~nm}, 1.0 \mu \mathrm{~J} /$ pulse, MeCN . (B) NIR probe fsTA spectra of $\mathrm{PTZ}^{+\bullet}$-DPA $\lambda_{\text {ex }}=900 \mathrm{~nm}, 1.0 \mu \mathrm{~J} /$ pulse, MeCN .


Figure S14. $\lambda_{\text {ex }}=517 \mathrm{~nm}, 1.0 \mu \mathrm{~J} /$ pulse, MeCN . (A) fsTA spectra of $\mathrm{PTZ}^{+\cdot}$-ACN. (B) Species-associated spectra obtained by global fitting. (C) Transient kinetics at selected wavelengths. (D) Populations of the transient species.

$$
k=\left[\begin{array}{ccc}
-\boldsymbol{k}_{A \rightarrow B} & 0 & 0 \\
\boldsymbol{k}_{A \rightarrow B} & -\boldsymbol{k}_{B \rightarrow G S} & 0 \\
0 & 0 & -\boldsymbol{k}_{C \rightarrow G S}
\end{array}\right]
$$

Initial populations: $\mathrm{A}_{0}=1, \mathrm{~B}_{0}=0$, and $\mathrm{C}_{0}=1$

Following excitation of $\mathrm{PTZ}^{+}-\mathrm{ACN}$ at $\lambda_{\text {ex }}=517 \mathrm{~nm}$, a broad absorptive feature between $\lambda=600$ and 700 nm , the region, where oxidized anthracenes typically absorb, ${ }^{9}$ is apparent after a delay of 0.6 ps (Figures 6A and S14A). This feature decays rapidly and a feature resembling the ${ }^{2 *} \mathrm{PTZ}^{+\bullet}$ ESA remains, which then undergoes a hypsochromic shift before decaying completely by a delay of 60 ps (Figure 6A and S14A). When the sample was irradiated with a $\lambda_{\mathrm{ex}}=900 \mathrm{~nm}$ excitation
pulse, $\mathrm{PTZ}^{+\cdot} \mathrm{GSB}$ and ESA are apparent after a 0.6 ps delay, but no broad feature between $\lambda=600$ and 700 nm is observed (Figures 6 C and S15A). The ${ }^{2 *}$ PTZ + • ESA undergoes the usual hypsochromic shift before decaying completely. No broad anthracene feature between $\lambda=600$ and 700 nm is observed.


Figure S15. $\lambda_{\text {ex }}=900 \mathrm{~nm}, 1.0 \mu \mathrm{~J} /$ pulse, MeCN. (A) fsTA spectra of $\mathrm{PTZ}^{+\cdot}$-ACN. (B) Species-associated spectra obtained by global fitting. (C) Transient kinetics at selected wavelengths. (D) Populations of the transient species.

$$
k=\left[\begin{array}{cc}
-\boldsymbol{k}_{A \rightarrow G S} & 0 \\
\boldsymbol{k}_{A \rightarrow B} & -\boldsymbol{k}_{B \rightarrow G S}
\end{array}\right]
$$

Initial populations: $\mathrm{A}_{0}=1$ and $\mathrm{B}_{0}=0$


Figure S16. (A) NIR probe fsTA spectra of $\mathrm{PTZ}^{+\bullet}-\mathrm{ACN} \lambda_{\mathrm{ex}}=517 \mathrm{~nm}, 1.0 \mu \mathrm{~J} /$ pulse, MeCN . (B) NIR probe fsTA spectra of $\mathrm{PTZ}^{+\bullet}-\mathrm{DPA} \lambda_{\mathrm{ex}}=900 \mathrm{~nm}, 1.0 \mu \mathrm{~J} /$ pulse, MeCN ..

## 5. Raman Spectroscopy



Figure S17. (A) Steady-state FSRS spectrum of a solution of $\mathrm{PTZ}^{\bullet+}$ in $\mathrm{MeCN}(d-3)$ obtained with a $540 \mathrm{~nm}(\sim 1$ ps, $0.7 \mu \mathrm{~J}$ ) Raman pump. (B) Computed normal modes.

The steady-state FSRS spectrum collected with Raman pump centered at $\lambda_{\mathrm{RP}}=540 \mathrm{~nm}$ provides the resonance Raman spectrum for the $\mathrm{PTZ}^{+} \mathrm{D}_{0}$ state and shows multiple features from $200-700 \mathrm{~cm}^{-1}$ and $1000-1600 \mathrm{~cm}^{-1}$ (Figure S15A). It is reproduced reasonably well by the normal mode analysis (Figure S15B) and is consistent with previously reported time-resolved resonance Raman spectra. ${ }^{11}$ The calculated $\mathrm{PTZ}^{+\cdot}$ spectrum was optimized in Gaussian 09 at CAMB3LYP/ $6-311+G(d, p)$ level of theory with tight convergence criteria on the forces and step sizes. Taking the optimized geometry, the Raman spectrum was computed at the same level of theory. The computed frequencies were scaled by an empirical factor of $0.951 .{ }^{12}$ The intensities in both the experimental and computed Raman spectra (Figure S15) have been normalized for a clearer comparison.

Addition of an actinic pump at $\lambda=515 \mathrm{~nm}$ promotes a portion of the sample to an excited electronic state, which is subsequently probed with $\lambda_{\mathrm{RP}}=400 \mathrm{~nm}$ to collect the resonance Raman spectrum of the excited electronic state at various time delays (Figure S16A). A single weak transient feature is observed at $1346 \mathrm{~cm}^{-1}$ upon excitation and no new features appear as it decays. The $1346 \mathrm{~cm}^{-1}$ feature likely represents a normal mode similar to the calculated $1290 \mathrm{~cm}^{-}$ ${ }^{1}$ ring deformation mode (Figure S16B). Both the amplitude and the numerical area of the 1346 $\mathrm{cm}^{-1}$ feature were found to decay monoexponentially with $\tau \sim 35 \mathrm{ps}$ (Figure S16C-E). These observations suggest that the transient population is decaying from the electronic excited state back to the electronic ground state with $\tau \sim 35 \mathrm{ps}$. Additionally, the centroid of the $1346 \mathrm{~cm}^{-1}$ feature appears to undergo a small shift to higher frequencies around $\Delta \mathrm{t} \sim 10 \mathrm{ps}$ (Figure S16F). This shift is consistent with the fast process observed in the fsTA experiment representing relaxation along the excited electronic potential energy surface.


Figure S18. $\lambda_{\mathrm{ex}}=515 \mathrm{~nm}(<100 \mathrm{fs}, 1 \mu \mathrm{~J}), \lambda_{\mathrm{RP}}=400 \mathrm{~nm}(\sim 1 \mathrm{ps}, 0.7 \mu \mathrm{~J}), \mathrm{CD}_{3} \mathrm{CN}(\mathrm{A})$ Time-resolved FSRS spectra of $\mathrm{PTZ}^{\bullet+}$. (B) Nearest calculated mode in $\mathrm{D}_{0}$. (C) Decay-associated spectra and (D) kinetics overlaid with fit following SVD analysis and global fitting to an exponential decay convoluted with a Gaussian instrument response. (E) Numerical area for $1300-1390 \mathrm{~cm}^{-1}$ overlaid with fit to the sum of an exponential decay and a step function convoluted with a Gaussian instrument response. (F) Centroid for $1300-1390 \mathrm{~cm}^{-1}$.

Table S1. Experimental and Computational Raman Frequencies and mode displacements.

| Raman Frequency ( $\mathrm{cm}^{-1}$ ) |  | Mode Displacement |
| :---: | :---: | :---: |
| Experiment | Computation |  |
| 291 | 446 |  |
| 375 | 517 |  |
| 501 | 588 |  |
| 668 | 762 |  |
| 1045 | 1120 |  |
| 1103 | 1156 |  |


| 1261 | 1193 |  |
| :---: | :---: | :---: |
| 1299 | 1236 |  |
| 1348 | 1290 |  |
| 1484 | 1429 |  |
| 1586 | 1569 |  |

## 6. Computational Section

Coordinates of optimized $\mathrm{PTZ}^{+\bullet}$
$\begin{array}{lllll}\text { C } & -7.62215900 & -3.65967500 & 0.13553800\end{array}$
C $\quad-6.51910800 \quad-3.46843500 \quad-0.69148600$
$\begin{array}{lllll}\text { C } & -5.83402900 & -2.24382200 & -0.67287900\end{array}$

| C | -6.30559800 | $-1.18885000$ | 0.14335700 |
| :---: | :---: | :---: | :---: |
| C | -7.38584000 | $-1.41416000$ | 1.01538100 |
| C | -8.03706300 | $-2.64242700$ | 1.00904500 |
| C | -4.22861700 | 0.02499300 | 0.16494800 |
| C | -3.52490900 | $-0.90004300$ | $-0.64160100$ |
| C | -2.12160000 | $-0.90504400$ | -0.62991900 |
| H | -1.57804600 | -1.61025900 | $-1.26261300$ |
| C | -1.43177600 | $-0.04125500$ | 0.21612500 |
| C | -2.13202400 | 0.82062800 | 1.07514100 |
| C | -3.52113100 | 0.85783000 | 1.05109400 |
| H | -8.14061800 | -4.62102200 | 0.12795100 |
| H | -6.16114100 | -4.27780900 | $-1.33153600$ |
| H | -7.69380800 | -0.62779900 | 1.70529800 |
| H | -8.86718000 | $-2.81390800$ | 1.69751900 |
| H | -0.33977900 | -0.06295100 | 0.23295700 |
| H | -1.58905300 | 1.45977000 | 1.77458000 |
| H | -4.07083200 | 1.51650500 | 1.72477900 |
| N | -5.64853900 | 0.07365900 | 0.07538500 |
| S | -4.39022400 | -2.04530400 | -1.66715700 |
| C | -6.33604100 | 1.26878700 | -0.17214000 |
| C | -5.62467700 | 2.48367600 | -0.38789000 |
| C | -7.75374900 | 1.28916000 | -0.30044500 |
| C | -6.30887500 | 3.66378900 | -0.64056600 |


| H | -4.53770700 | 2.50204200 | -0.38866600 |
| :--- | :--- | :--- | :--- |
| C | -8.41881900 | 2.48015900 | -0.55322000 |
| H | -8.33585800 | 0.37476700 | -0.22484000 |
| C | -7.70937600 | 3.67999100 | -0.70869800 |
| H | -5.74065400 | 4.58206600 | -0.80409800 |
| H | -9.50709400 | 2.47045400 | -0.64471400 |
| H | -8.24117500 | 4.61290400 | -0.90879200 |

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