

Supporting Information for:

Rapid, “Step Capture” of Holes in Chloroform During Pulse Radiolysis

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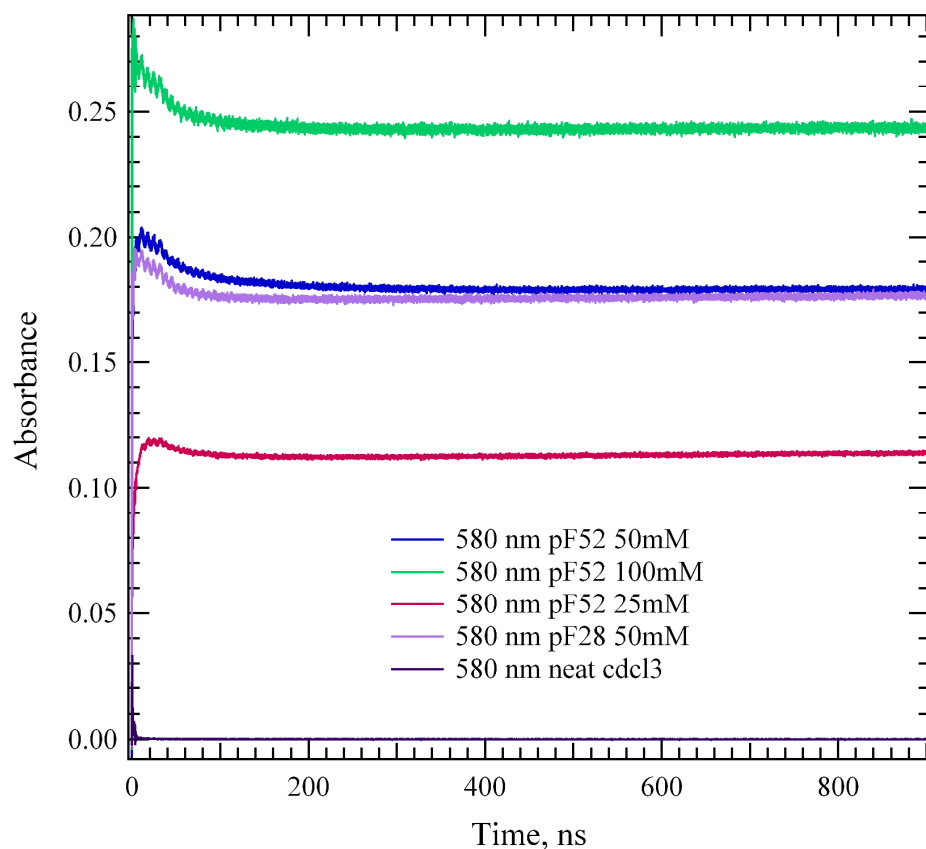


Figure S1. Absorptions at 580 nm produced in the first few ns with samples containing pFs do not decay appreciably at times as long as $\sim 1 \mu\text{s}$. The species responsible is primarily the $[\text{pF}^+, \text{Cl}^-]$ ion pair, formed following recombination. The initial decay may be due to an absorption spectral shift or molar extinction coefficient change upon ion-pairing; a fraction may also be due to decay of triplets observed at 780 nm that still weakly absorb at 580 nm.

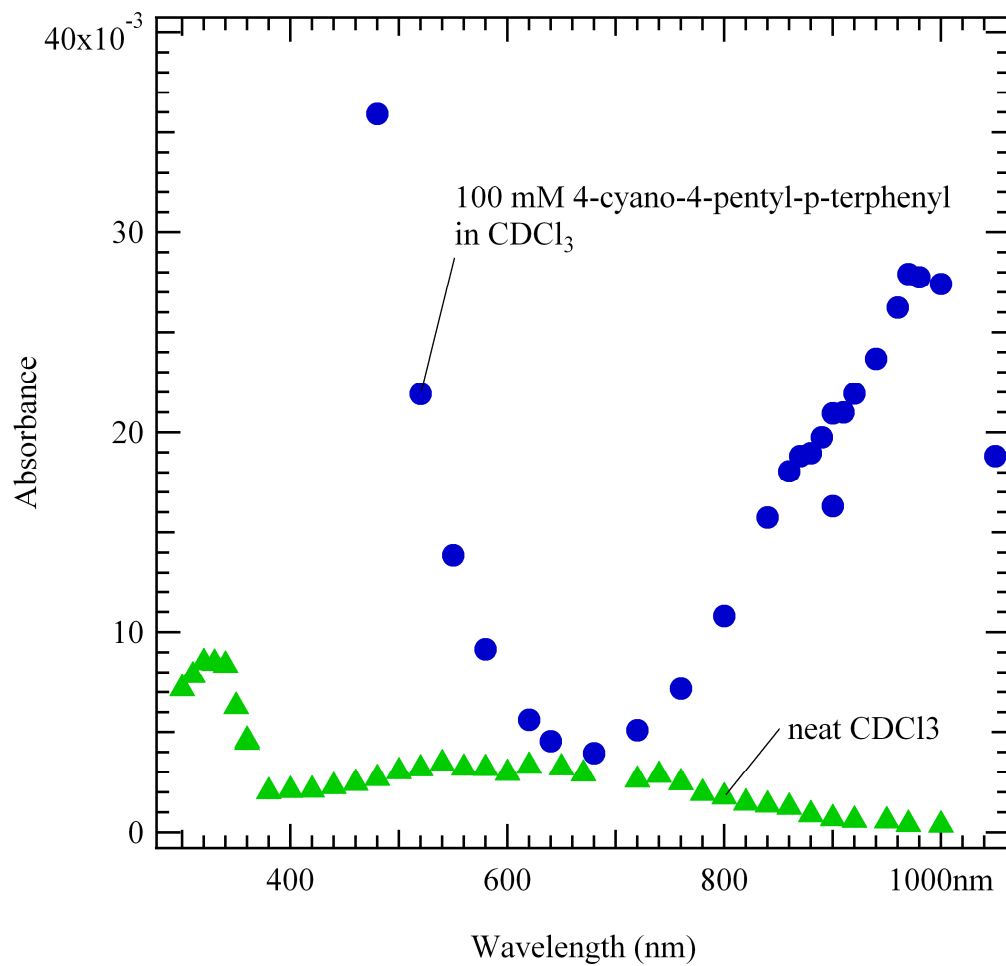


Figure S2. Absorption spectrum of 4-pentyl-4''-cyano-p-terphenyl measured in CDCl₃ at 1 ns after radiolysis. The strong and broad absorption is nearly identical to that of p-terphenyl radical; cation, which has a maximum near 965 nm.^{42,43}

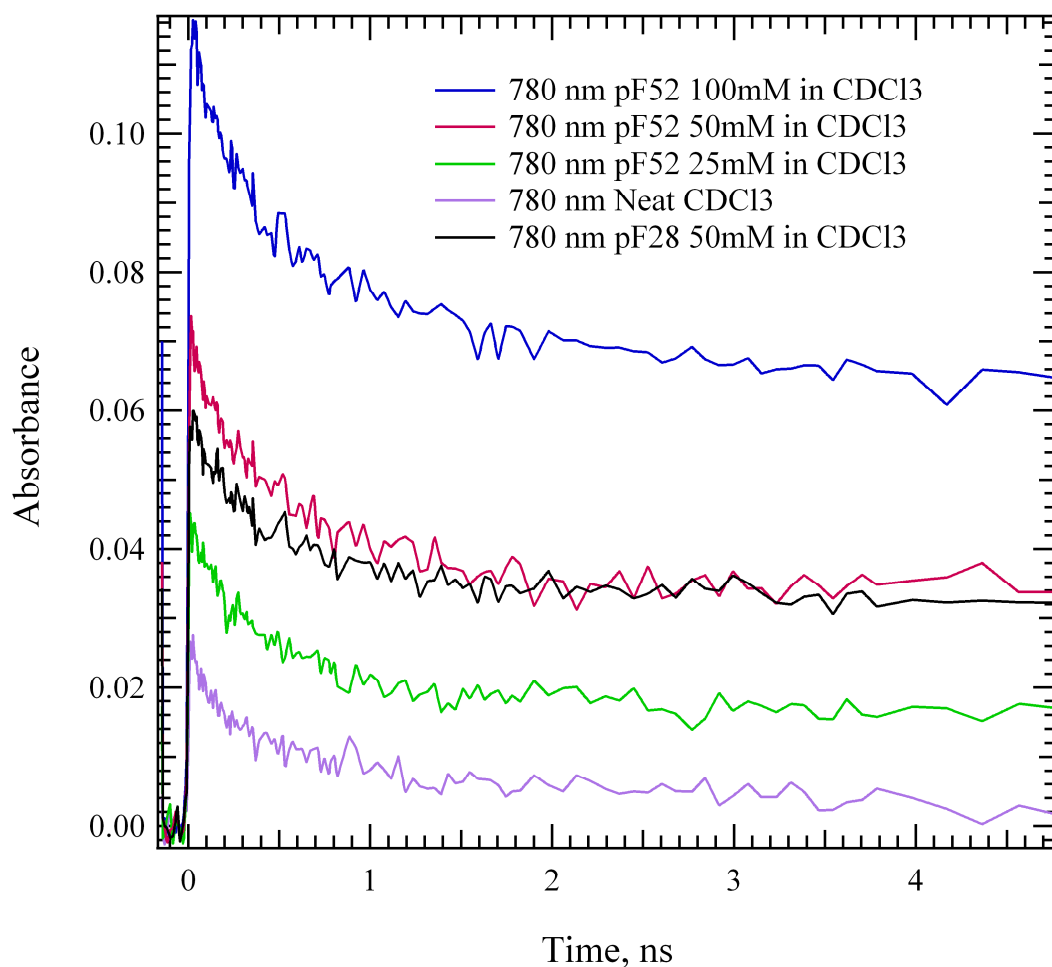


Figure S3. Transient absorption at 780 nm, near the peaks of the $^1\text{pF}^*$ and $^3\text{pF}^*$ spectra.

Polymer concentrations are in repeat units. Excited states can be produced by Cerenkov absorption, excitation by high energy electrons, and recombination of charges. Observed ~ 0.4 ns decays are consistent with $^1\text{pF}^*$ decay; the increased non-decaying component with $[\text{pF}]$ on this timescale is reasonably due to $^3\text{pF}^*$.

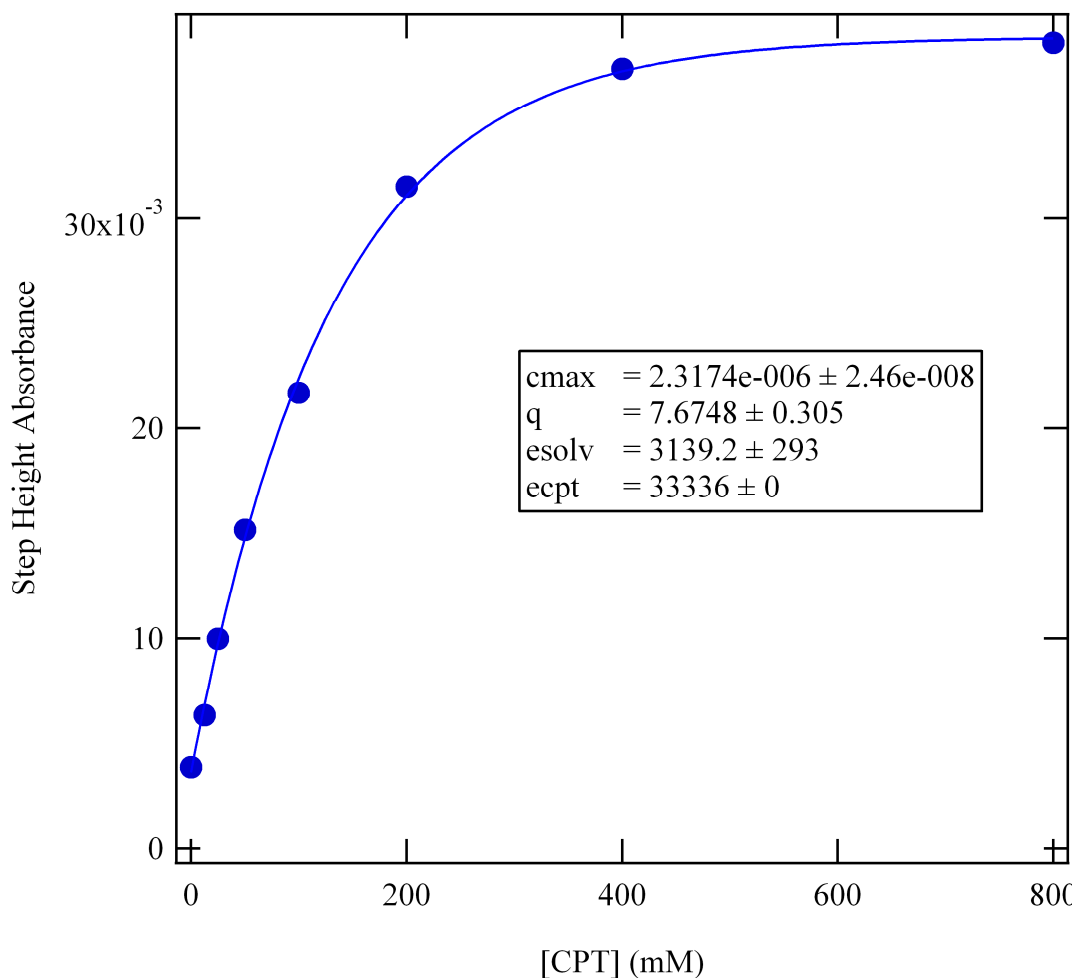


Figure S4. Fit to raw step heights measured in varying concentrations of CPT at 900 nm. Fit function explicitly includes contribution of the solvent species:

$$\text{Step height} = c_{\max} \left[\epsilon_{\text{CPT}} (1 - e^{-qc}) + \epsilon_{\text{solv}} e^{-qc} \right]$$

Where c_{\max} is the maximum concentration of $\text{CPT}^{+\bullet}$ that can be formed and is equal to the initial concentration of $\text{CDCl}_3^{+\bullet}$; $\epsilon_{\text{CPT}} = 39,650 \text{ M}^{-1} \text{ cm}^{-1}$ for $\text{CPT}^{+\bullet}$ at 965 nm, scaled to 900 nm where the data was collected; ϵ_{solv} is the extinction coefficient of the solvent species at 900 nm, q is the quencher coefficient, and $c = [\text{CPT}]$.