

## Electronic Supplementary Information

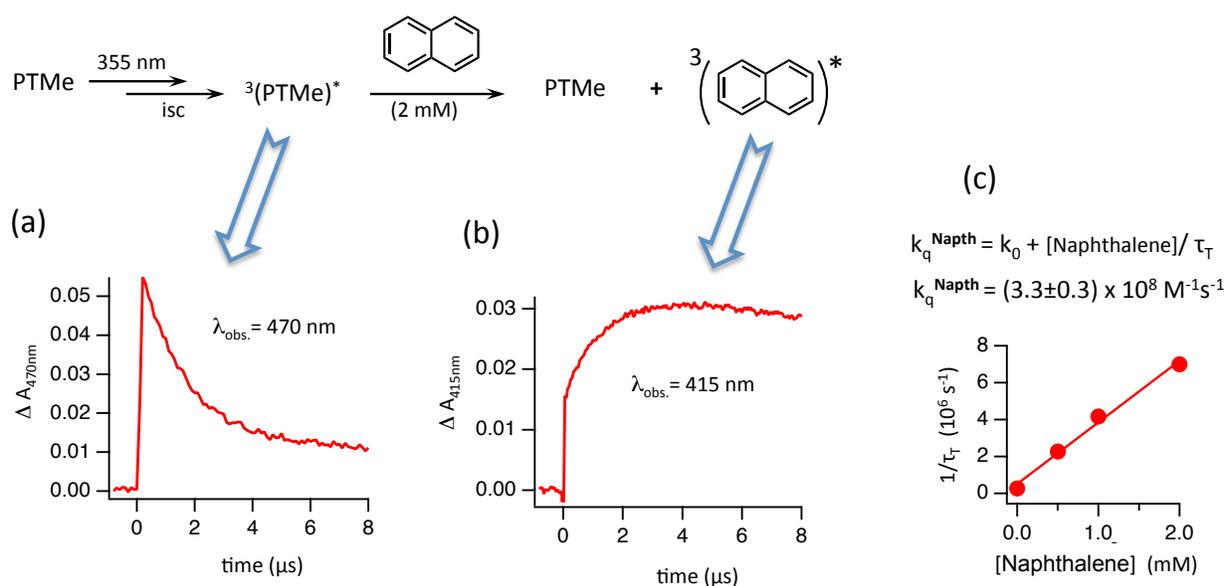
### The Active Role of Excited States of Phenothiazines in Photoinduced Metal Free

### Atom Transfer Radical Polymerization: Singlet or Triplet Excited States?

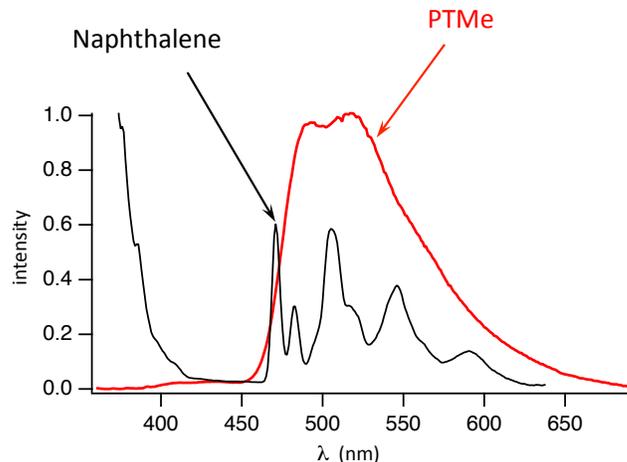
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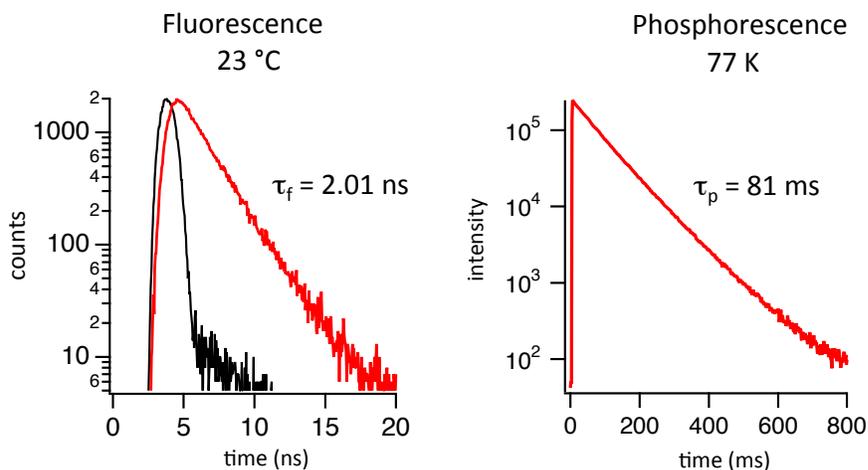
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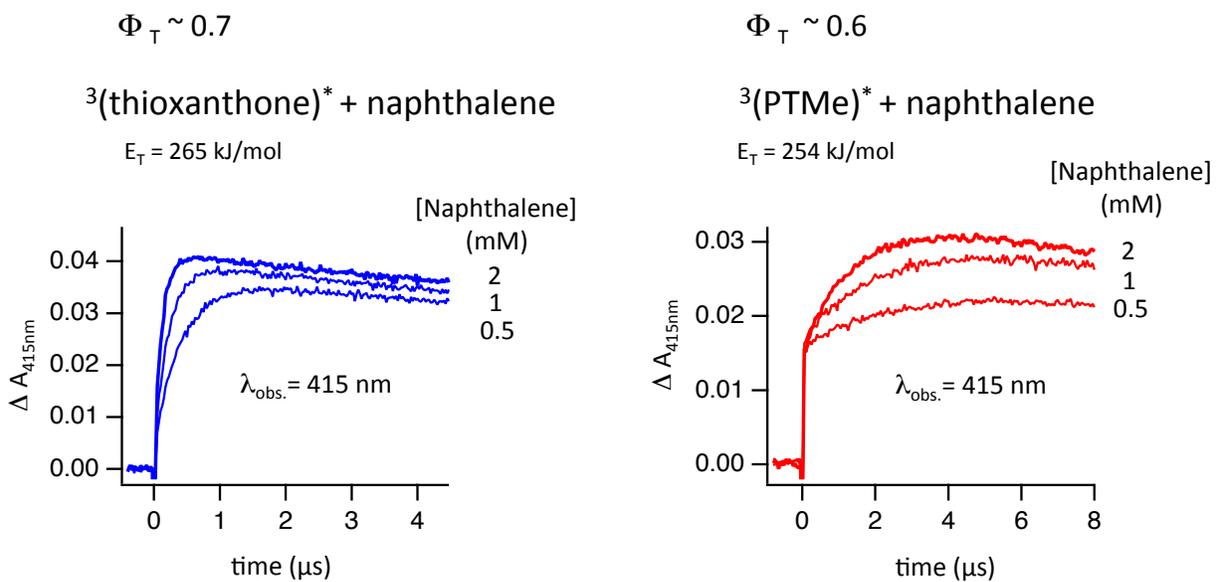
**Fig. S1** Transient absorption decay traces monitored at 470 nm (a) and 415 nm (b) following laser excitation ( $\lambda_{\text{ex}} = 355 \text{ nm}$ , 7 ns pulse width) of PTMe in the presence of 2 mM naphthalene in argon saturated DMA solutions, and plot of inverse PTMe triplet lifetime vs. varying naphthalene concentrations (c) in argon saturated DMA solutions.



**Fig. S2** Phosphorescence spectra of PTMe ( $\lambda_{\text{ex}} = 350 \text{ nm}$ ) and naphthalene ( $\lambda_{\text{ex}} = 300 \text{ nm}$ ) in DMA at 77K. The triplet energy of naphthalene in DMA was determined from the first peak of phosphorescence ( $E_T = 254 \text{ kJ/mol}$ ). Because of the broad, structureless PTMe phosphorescence, the exact value of the triplet energy is not clear, but should be close to 254 kJ/mol.



**Fig. S3** Left: Fluorescence decay (red) of PTMe in DMA at 23 °C with 350 nm excitation monitored at 450 nm. Instruments response function (black). Right: Phosphorescence decay of PTMe in DMA at 77 K with 350 nm excitation monitored at 490 nm.



**Fig. S4** Transient absorption decay traces monitored at 415 nm (naphthalene triplet) following laser excitation ( $\lambda_{\text{ex}} = 355 \text{ nm}$ , 7 ns pulse width) of thioxanthone (left) or PTMe (right) in the presence of varying amounts of naphthalene in argon saturated DMA solutions.