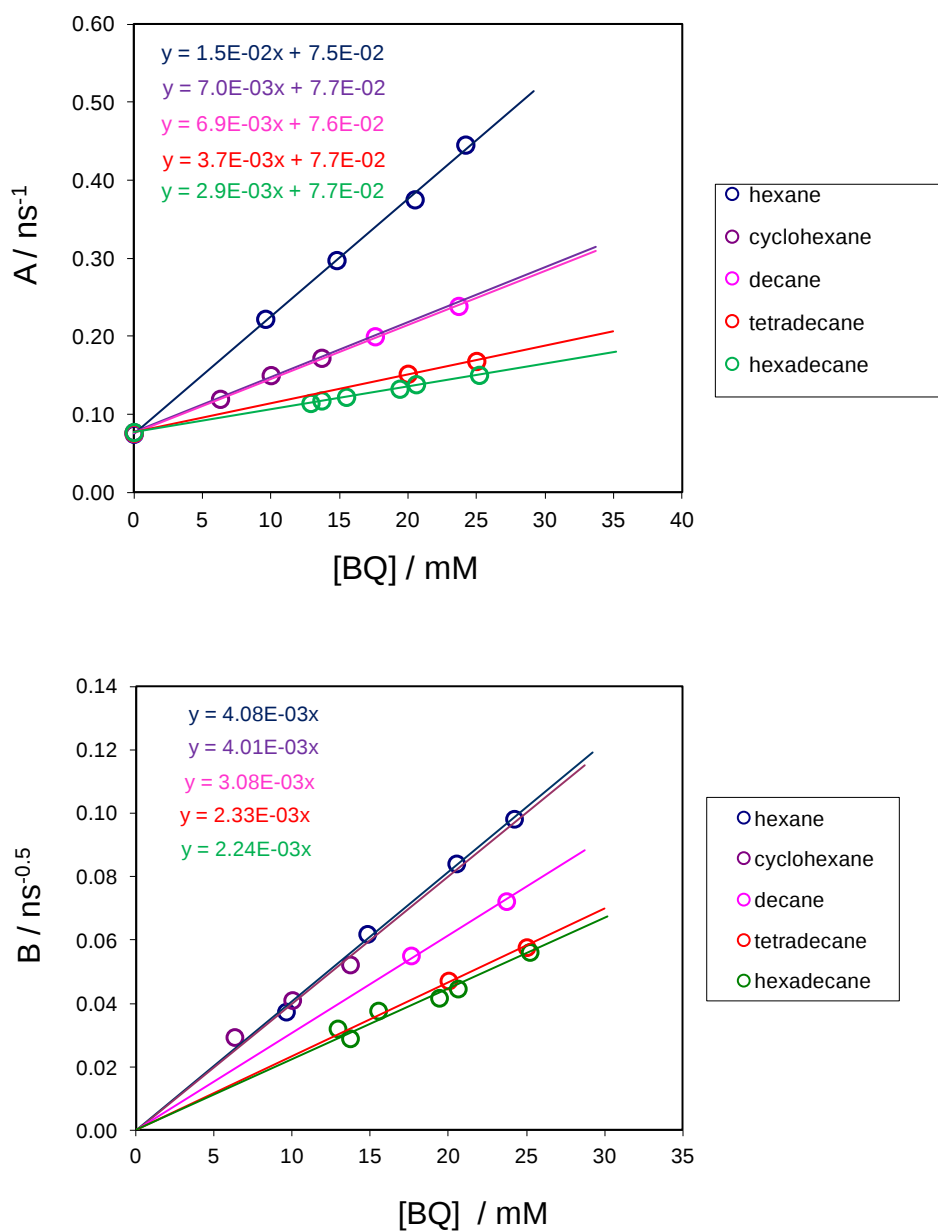


Supporting Information

Diffusion-Facilitated Direct Determination of Intrinsic Parameters for Rapid Photoinduced Bimolecular Electron-Transfer Reactions in Nonpolar Solvents

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The A and B values obtained from the analysis according to Equation 9 are plotted in Figure S1.



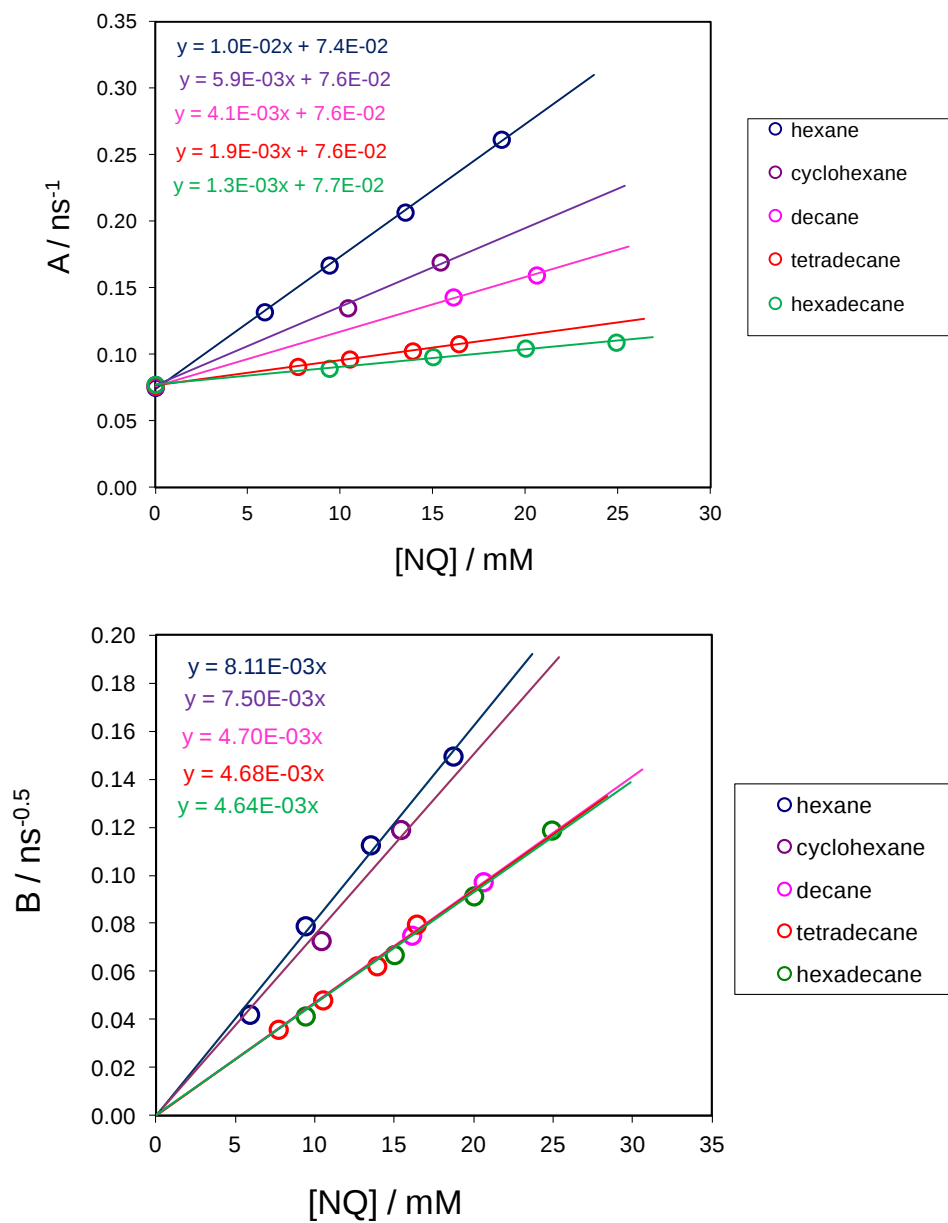


Figure S1. Results of fluorescence decay curve analysis at 298.2K, according to Equation 9.

Absorption and fluorescence spectra

In order to see if we find any interaction between the reactants spectroscopically, we have measured absorption and fluorescence spectra for solutions containing only TPP, BQ, or NQ (Figure S2) and for those containing both TPP and one of the quinones (Figure S3). From the absorption spectra, we see no interactions between TPP and quinones; although not shown here, there is no evidence of absorption in the range 650-1100nm.

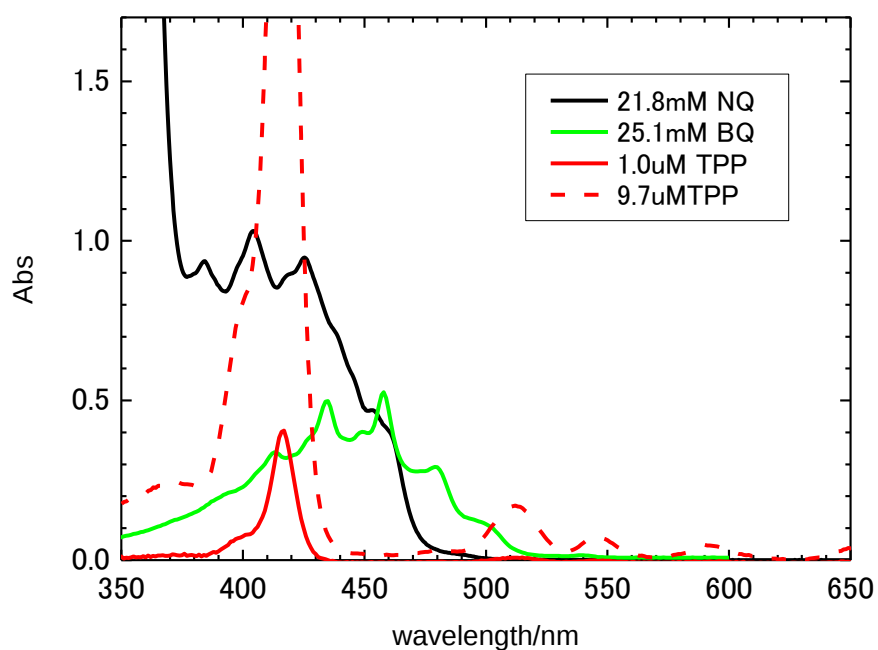


Figure S2. Absorption spectra of 1 μ M TPP, 21.8mM BQ, and 25.1mM NQ in hexadecane.

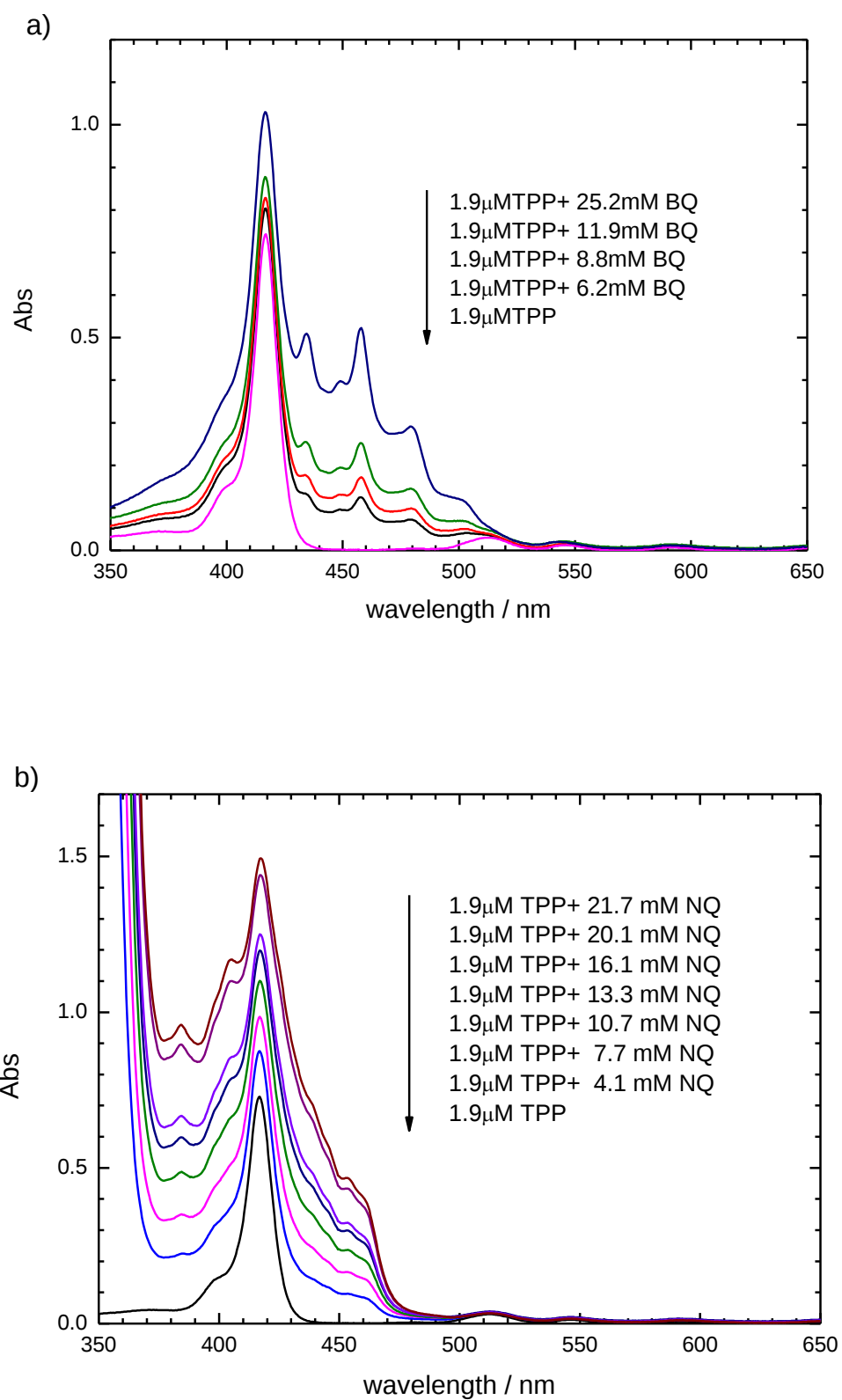


Figure S3. Absorption spectra of 1.9 μ M TPP and various concentrations of (a) BQ or (b) NQ in hexadecane.

Steady-state fluorescence quenching results

According to Rosspeintner et al. (ref. 1), dependence of the steady-state fluorescence intensity Φ on the quencher concentration is expressed as:

$$\frac{\Phi(0)}{\Phi(c)} = \frac{\int_0^\infty I(t,0)dt}{\int_0^\infty I(t,c)dt} = 1 + \kappa(c)\tau_0 c \quad (\text{S1})$$

where $\kappa(c)$ is the steady-state quenching rate coefficient as a function of quencher concentration, c , and τ_0 is the fluorescence lifetime at $c=0$.

Steady-state fluorescence measurements were made using a fluorescence spectrophotometer (Hitachi F-7000) by circulating temperature-controlled water in the cell holder. In the case of the time-resolved fluorescence measurements, TPP was excited at 417nm. However, since both BQ and NQ absorb 417nm light, large corrections are necessary to obtain the $\Phi(0)/\Phi(c)$ values, and so in the case of steady-state fluorescence measurements TPP was excited at 512nm where BQ absorb some but NQ absorb no excitation light. Furthermore, because the molar absorption coefficient of TPP at 512nm is substantially smaller than at 417nm, it was necessary to use 10 μ M TPP solutions for the steady-state measurements (c.f. 1 μ M TPP for time-resolved measurements). The fluorescence spectrum of TPP was found to be independent of excitation at 417nm and 512nm, and also at 1 μ M and 10 μ M TPP concentration. Figure S4 shows the fluorescence spectra of TPP at various concentrations of BQ and NQ.

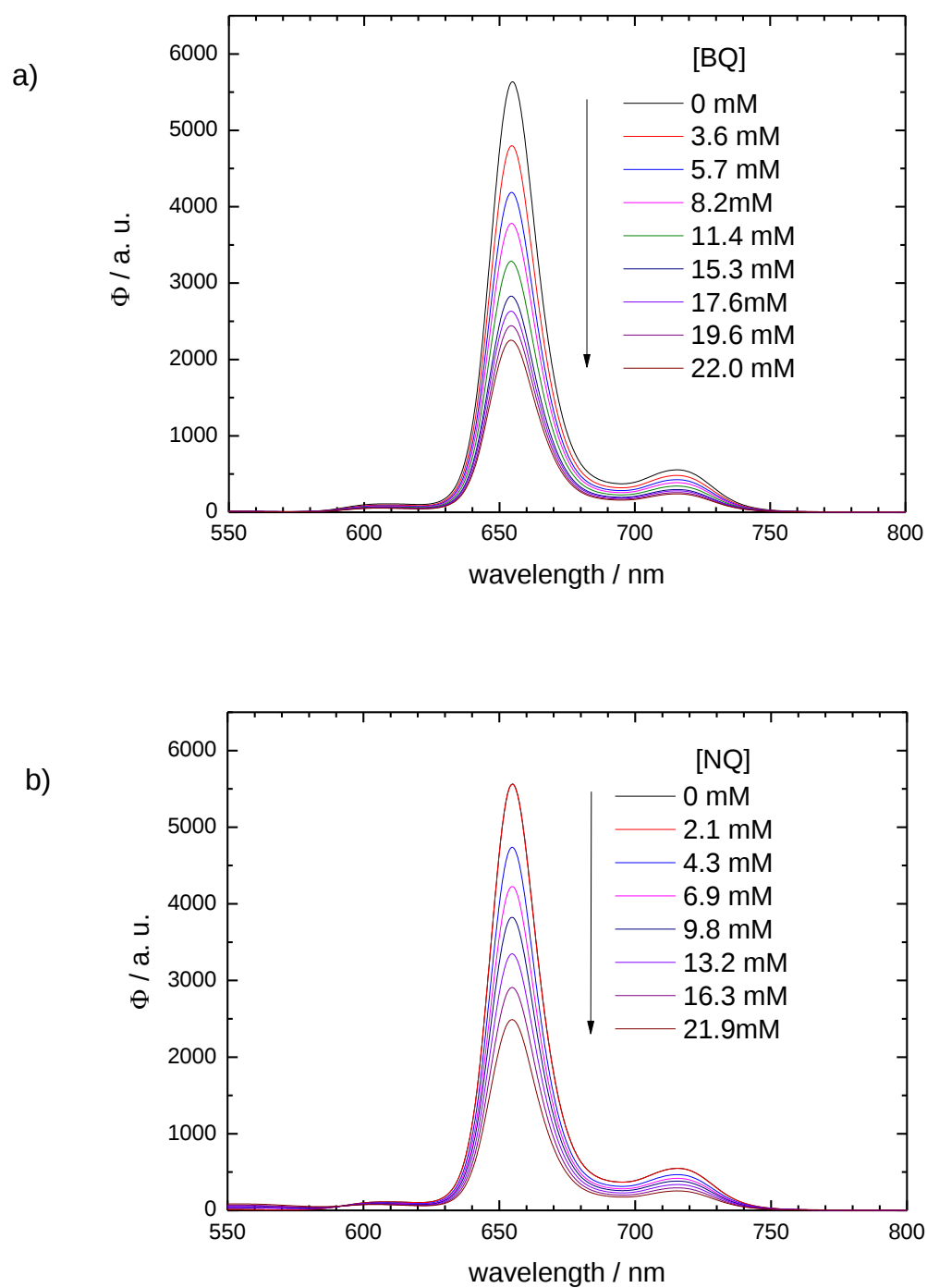


Figure S4. Fluorescence spectra of 10 μ M TPP excited at 512nm as a function of concentration of (a) BQ and (b) NQ.

Figure S5 shows the steady-state quenching by BQ and NQ. The slope of the plots of $\Phi(0)/\Phi(c)$ vs c increases with increasing quencher concentration for both systems. As $c \rightarrow 0$, the slopes approach the values obtained from the time-resolved measurements.

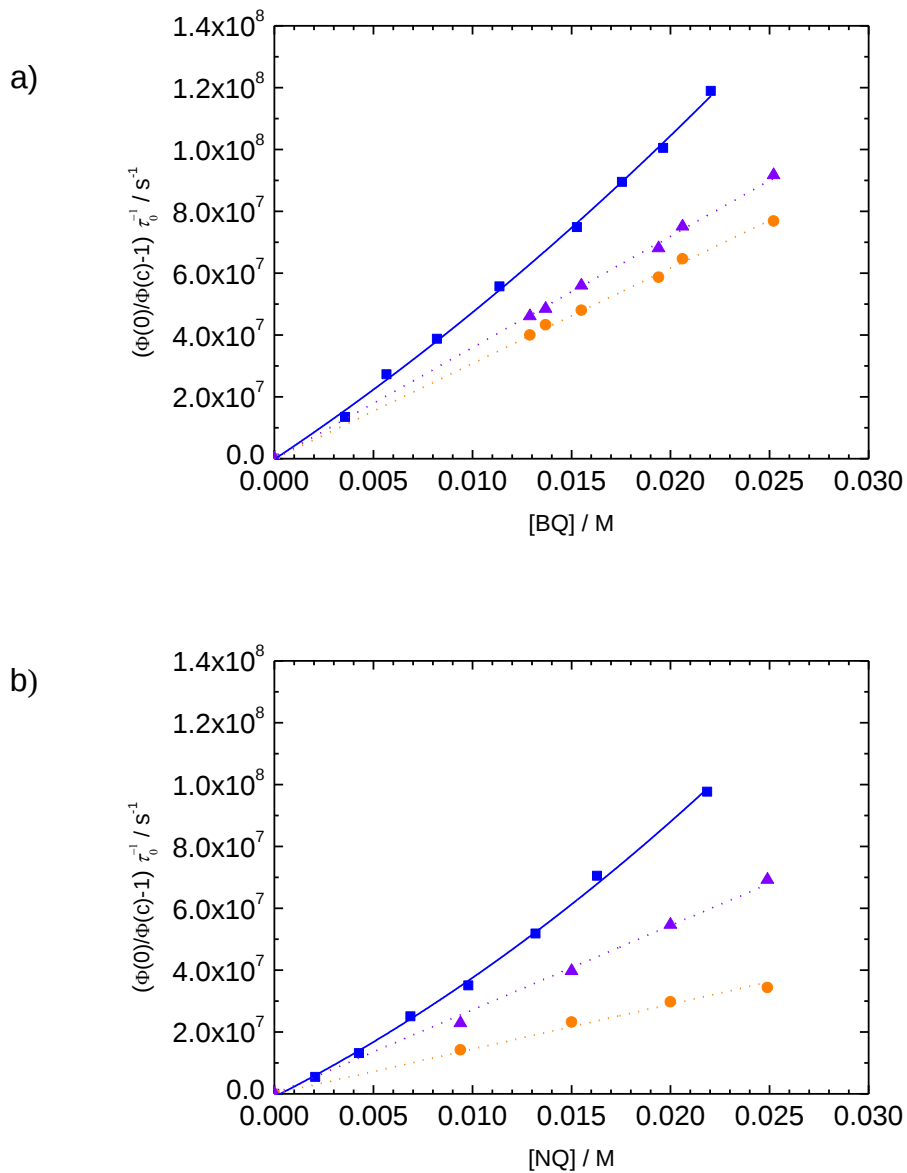


Figure S5. Steady-state fluorescence quenching of 10 μM TPP by BQ (a) and NQ (b). ■, $\Phi(0)/\Phi(c)$; ▲, $\int_0^\infty \exp(-A(0)t - B(0)t^{0.5}) dt / \int_0^\infty \exp(-A(c)t - B(c)t^{0.5}) dt$; ●, $\int_0^\infty \exp(-A(0)t) dt / \int_0^\infty \exp(-A(c)t) dt$. Dotted and solid lines are only a guide for the eye.

Figure S6 shows steady-state rate coefficients as a function of the quencher concentration. The magnitude of $\kappa(c)$ is expected to increase further with increasing quencher concentration, reflecting the fast (static) electron-transfer quenching process, ultimately reaching the intrinsic rate constant. However, we were unable to increase the quencher concentrations further due to solubility limitations. In the case of TPP-BQ, as seen in Figure S2, the high concentration of BQ absorb some excitation light (512nm), and the correction for so-called "inner-filter effect" (ref. 2) could affect the $k(c)$ value by 10% or less.

These steady-state quenching results suggest that the time-resolved measurements and analysis (at least in hexadecane at 25 °C) do not included quenching that occurs at timescales shorter than that of the time-resolved measurements in the present work; there is little, if any, influence of translational diffusion in this so-called "static" phase of the quenching process. Since the present work focuses on analysis of the "transient" phase of the quenching kinetics in order to investigate the effects of diffusion on the reaction rate without the need to assume bulk diffusion coefficients, the static quenching component will have little bearing on the reported findings.

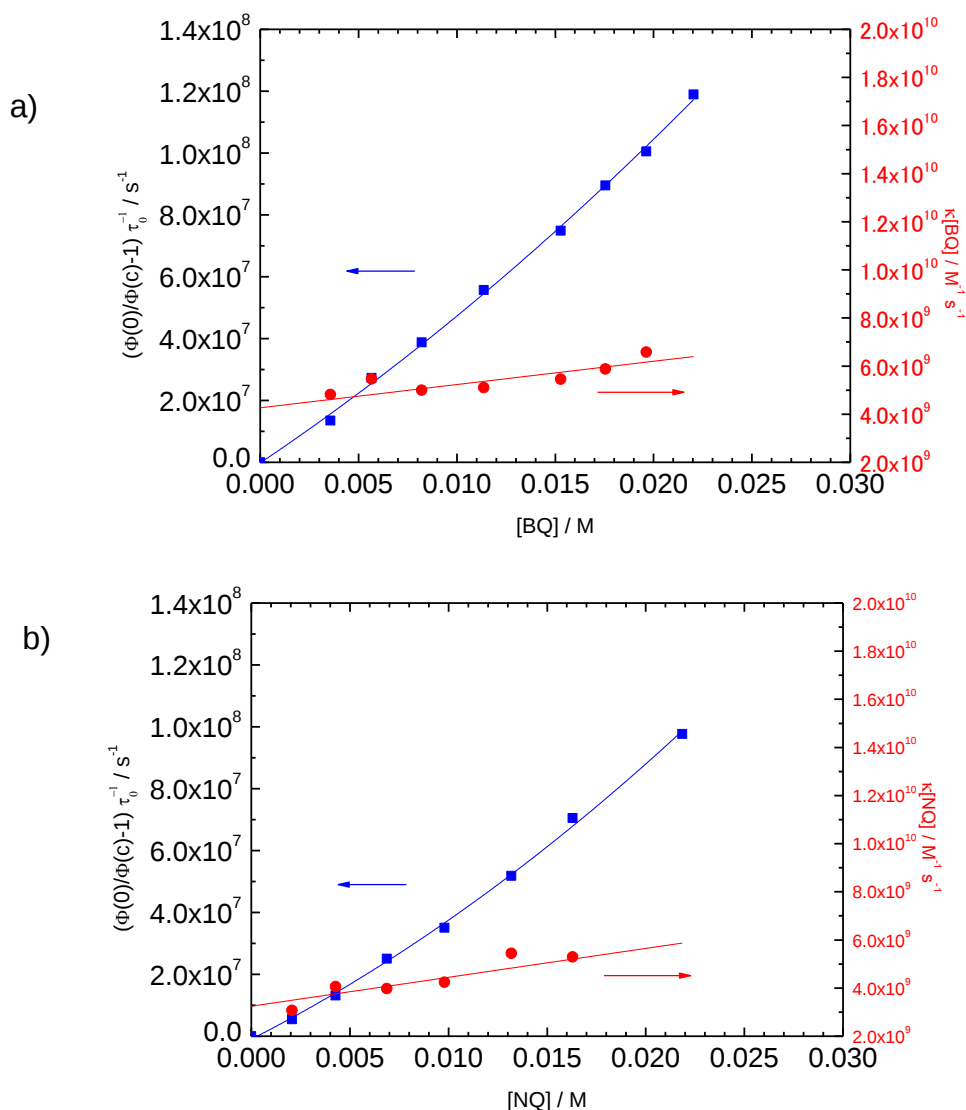


Figure S6. Steady-state fluorescence quenching and rate coefficients as a function of the quencher concentration. Solid lines are only a guide for the eye.

Exciplex formation computation

We calculated the structures and energies for TPP-Quinone exciplexes using the Gaussian 09 software with B3LYP/6-311+G**.³⁾ The results for structure optimizations are shown in Figures S7 and S8. The initial orientations are both parallel orientation with a center-to-center distance of 0.2 nm (Figure S7). The top and side views for TPP-BQ and TPP-NQ after energy optimization are shown in Figs S8(a) and 8(b), respectively. In the case of TPP-BQ, the separation distance increases keeping a parallel orientation, but in the case of TPP-NQ, their orientation is no longer parallel. Figure S9 shows the energy dependence on the separation

distance for TPP-BQ, where we see a very shallow minimum. In the case of TPP-NQ, however, our calculations do not show a minimum.

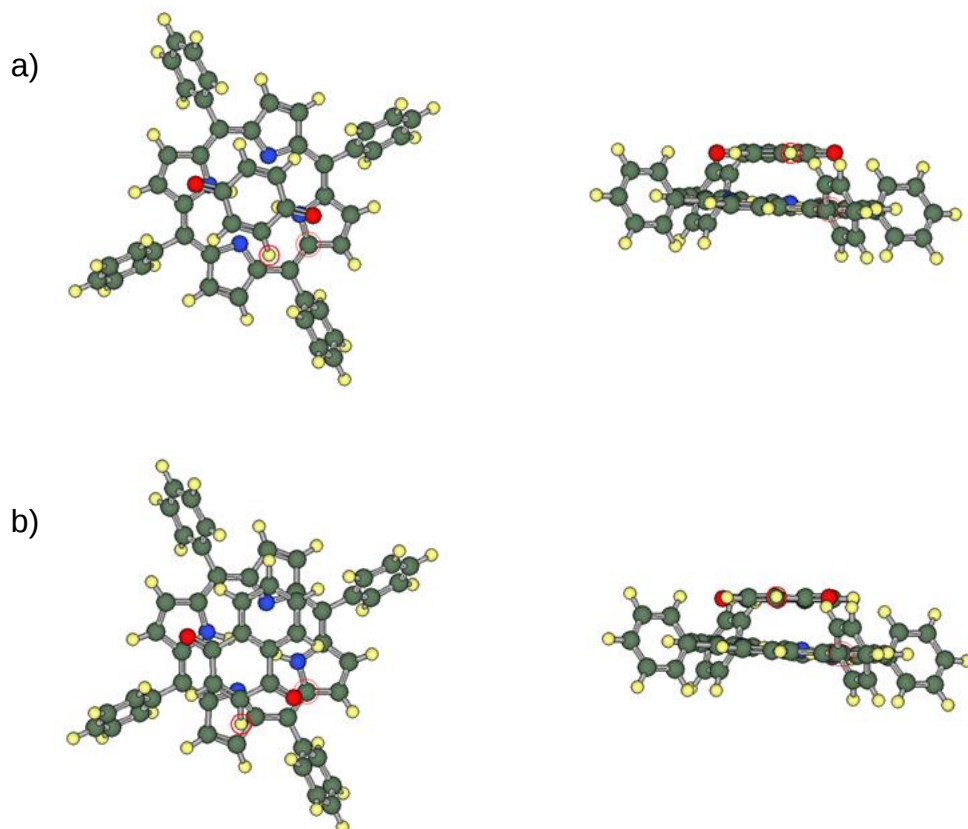


Figure S7. a) Top and side views for the TPP-BQ exciplex before energy-optimization, $L(\text{TPP-BQ}) = 0.2$ nm. b) Top and side views for the TPP-NQ exciplex before energy-optimization, $L(\text{TPP-NQ}) = 0.2$ nm.

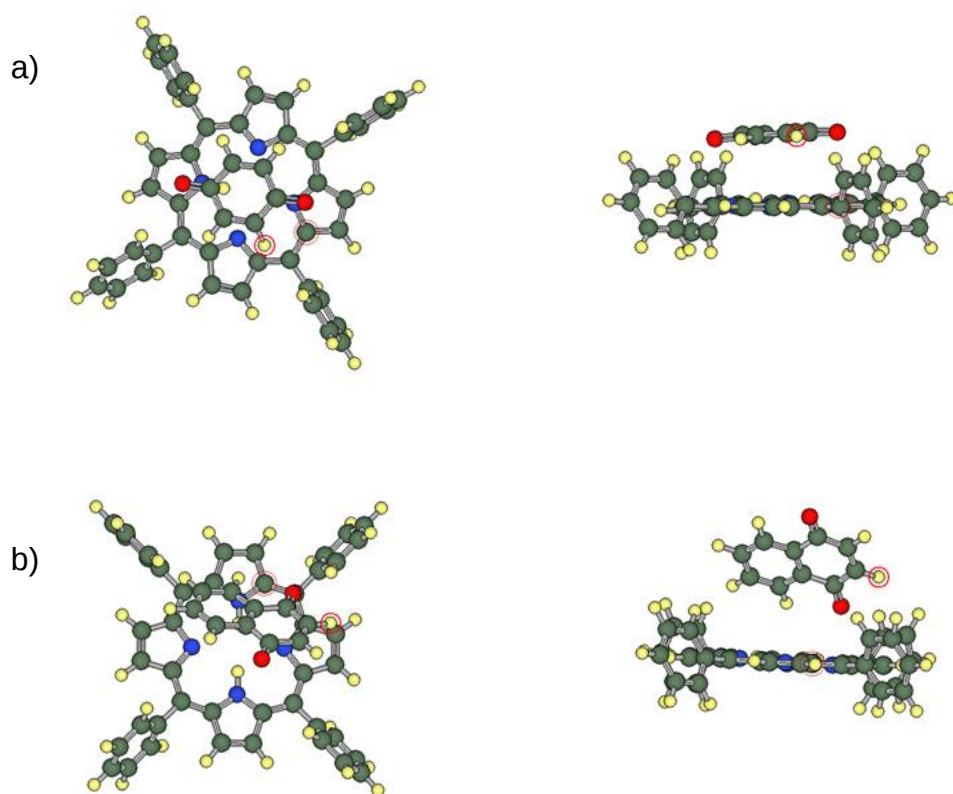


Figure S8. a) Top and side views for the TPP-BQ exciplex after energy-optimization, $L(N-O)=2.545\text{\AA}\rightarrow 3.346\text{\AA}$. b) Top and side views for the TPP-NQ exciplex after energy-optimization, $L(N-O)=2.271\text{\AA}\rightarrow 6.535\text{\AA}$.

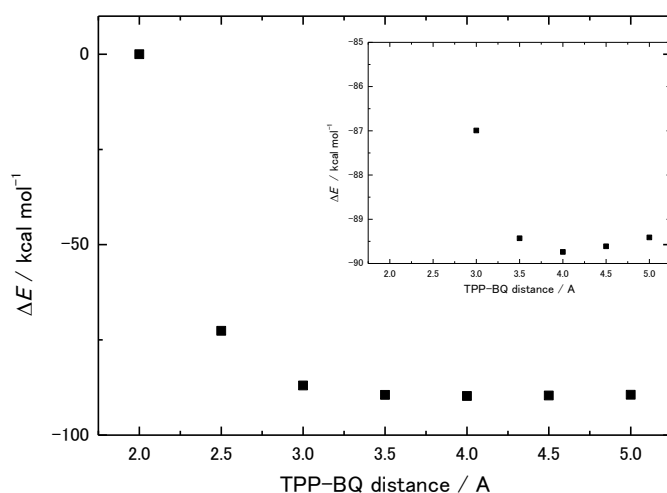


Figure S9. Distance potential curve for the TPP-BQ exciplex.

References

- 1) Rosspeintner, A.; Angulo, G.; Vauthey, E. Bimolecular Photoinduced Electron Transfer Beyond the Diffusion Limit: The Rehm–Weller Experiment Revisited with Femtosecond Time Resolution. *J. Am. Chem. Soc.* **2014**, *136*, 2026–2032.
- 2) Kubista, M; Sjoback, R; Eriksson, S; Albinbinsson, B. Experimental Correction for the Inner-filter Effect in Fluorescence Spectra. *Analyst*, **1994**, *119*, 417-419.
- 3) Gaussian 09, Revision C.01, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, M. J.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2009.