Supporting Information

for

Quantum coherence enhances electron transfer rates to two equivalent electron acceptors

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1. Methods and instrumentation

1.1 Synthesis and characterization

Reagents and solvents were purchased from commercial sources and used as received unless otherwise noted. Column chromatography was performed on standard silica gel, 60 angstrom, 32-63 µm (Sorbent Technologies). ¹H and ¹³C NMR spectra were recorded on a Varian 500 MHz spectrometer at room temperature. ¹H and ¹³C chemical shifts are listed in parts per million (ppm)
and are referenced to residual protons or carbons of the deuterated solvents. High resolution mass spectra (HRMS) were obtained with an Agilent LCTOOF 6200 series mass spectrometer using electrospray ionization (ESI) and atmospheric pressure photoionization (APPI).

1.2 Cyclic voltammetry

Cyclic voltammetry (CV) experiments were carried out at room temperature in argon-purged solutions of tetrahydrofuran (THF) with a Gamry Multipurpose instrument (Reference 600) interfaced to a PC. All CV experiments were performed using Pt as the working and counter electrodes, Ag/AgCl as the reference electrode, and ferrocene as an internal standard. The concentration of the sample and supporting electrolyte, tetrabutylammonium hexafluorophosphate (TBAPF$_6$), were 1.0 mM and 0.1 M, respectively.

1.3 Steady-state optical spectroscopy

Steady-state UV-visible absorption spectra were collected using a Shimadzu UV-1800 spectrophotometer at 295 K with optical densities (OD) of ~0.5, <1 mM in 1,4-dioxane, in quartz cuvettes with a path length of 1 mm.

1.4 Time-resolved optical spectroscopy

Femtosecond transient absorption (TA) spectroscopy experiments were performed on a previously described 1 kHz Ti:sapphire regeneratively amplified laser system (Spectra-Physics Tsunami oscillator, Spitfire Pro amplifier). Specifically, <5% of the fundamental (1.50 eV (828 nm), ~100 fs, 1 mJ/pulse) was directed onto a delay stage before 2 μJ/pulse of the fundamental were focused into an uncoated 2 mm CaF$_2$ crystal (Newlight Photonics Inc.) cut along the <001> plane to generate a chirped broadband continuum (probe) pulse ranging from 1.55–3.76 eV (800–330 nm). The CaF$_2$ crystal was rastered 7.5 mm in one direction at 1.15 mm/s to avoid
thermal degradation. The probe pulse was split so that one portion provided a reference spectrum and the other portion interacted with the sample.

For the pump, 0.5 mJ/pulse of the fundamental was directed into a commercial non-collinear optical parametric amplifier (Light Conversion, TOPAS-White,) to generate the <50 fs excitation pulse centered at 3.49 or 3.37 eV (355 or 368 nm). The pump pulse was then directed through a CaF\(_2\) prism compressor in the folded geometry to compensate for the accumulated group delay dispersion before interaction with the sample. The apex-to-apex distance of the prism compressor was \(~250\) mm and \(~300\) mm during experiments performed at ambient and cryogenic temperatures, respectively. The pump pulse was then directed through a mechanical chopper (500 Hz) to block every other pulse. The pump pulse energy (200–500 nJ/pulse) was attenuated with an iris and then focused to \(~300\) \(\mu\)m diameter (\(~500\) \(\mu\)m during experiments performed at cryogenic temperatures to prevent sample degradation) at the sample. The polarization of the pump pulse after generation was parallel to the probe pulse (horizontal) and was not manipulated to reduce accumulated dispersion.

The signal probe, following interaction with the sample, and the reference probe were coupled into optical fibers and detected with a customized Helios spectrometer and recorded by the Helios software (Ultrafast Systems, LLC). The reported signals were calculated by averaging the shot-to-shot difference spectra as shown in eq S1, where \(S(\lambda,t)\) is the signal, \(T_{Sig}\) is the probe that interacts with the sample, \(T_{Ref}\) is the reference probe, and * indicates the pump pulse was present. The scattered light and group delay dispersion were corrected for using Surface Xplorer (Ultrafast Systems, LLC).

\[
S(\lambda,t) = \left[ -\log_{10}\left( \frac{T_{Sig}^{*}/T_{Ref}^{*}}{T_{Sig}/T_{Ref}} \right) \right] 
\]

(S1)
All samples were prepared as solutions with an OD of ~0.5 in a glovebox under nitrogen atmosphere to exclude oxygen. For experiments at ambient (295 K) temperature, samples were prepared in 1,4-dioxane in 1 mm quartz cuvettes and were stirred during TA experiments to minimize local heating and sample degradation. Reported TA spectra represent 1–1.5 s averaging per time delay and were measured on three separate days. For experiments at cryogenic (190 - 5.5 K) temperatures, samples were prepared in 2-methyltetrahydrofuran (Me-THF) in a <1 mm path length cell consisting of a front quartz window (0.75 mm thick), a PTFE o-ring spacer (~0.75 mm thick), and a rear quartz window (1.65 mm thick). The sample was mounted in a STVP-100 cryostat (Janis Research Company, LLC) between two copper plates to afford thermal contact for temperature monitoring and control using a Cryo-Con 32B temperature controller (Cryogenic Control Systems, Inc.). TA spectra were collected for samples at 90 and 5.5 K on three separate days at 3–5 spots in the glassy Me-THF matrix each day with 0.5 s averaging per time delay per spot to minimize the effects of local heating and sample degradation. TA spectra at the other reported cryogenic temperatures were collected at 2-4 spots in the glassy Me-THF matrix with 0.5 s averaging per time delay per spot.

1.5 Kinetic analysis

Analysis of the charge separation (CS) kinetics was accomplished using the TA data collected at cryogenic temperatures following subtraction of \( S(\lambda, t) \leq -1 \) ps resulting from scattered light and long-lived \(^3\text{An}^*\) population. Kinetic traces at select probe energies spanning the \(^1\text{An}^*\) excited-state absorption (ESA) were fit using Origin 2015 (OriginLab Corporation) with eq S2 which includes (i) the convolution of a Gaussian IRF of width \( w \) with the sum of a step function (\( S_0 \) before and \( S_0' \) after \( t_0 \)) and an exponential decay with amplitude \( A \) and time constant \( \tau \) to describe the dynamics following excitation of \(^1\text{An}^* \leftarrow S_0\) and (ii) the sum of a Gaussian of width \( w \) and the first two
derivatives with amplitudes $B_i$ to capture the pump and probe cross-correlation (x-corr) resulting from the optical Kerr effect (OKE) response of the sample medium and quartz cuvette/windows (given by the Dirac delta function, $\delta(t - t_0)$, and its first two derivatives). The time resolution is given by the FWHM of the Gaussian instrument response function (IRF), $\tau_{IRF} = 2w\sqrt{\ln 2}$, which was <100 fs at these probe energies (vide infra).

$$S(t) = e^{-\frac{t^2}{2w^2}} \left\{ S_0 + \sum_{i=0}^{2} B_i \frac{d}{dt} \left[ \delta(t - t_0) \right] + Ae^{-\frac{(t-t_0)}{\tau}} \right\}$$ \hspace{1cm} (S2)

The kinetic parameters, $t_0$, $w$, $\tau$, $A$, $B_i$, $S_0$, and $S_0'$ were fit independently at each probe energy to account for the probe energy dependence of $t_0$, $w$, $A$, and $B_i$. For samples at 90 and 5.5 K, $\langle \tau \rangle \pm 1\sigma$ was calculated as the average and standard deviation, respectively, of the $\tau$s resulting from fits at 5–7 probe energies for 2–6 experiments on 3 separate days. For samples at other cryogenic temperatures, $\langle \tau \rangle \pm 1\sigma$ was calculated using the $\tau$s from fits at 2–7 probe energies for 2–4 experiments. It is worth noting that averaging the $\tau$s resulting from fits either (i) at any single selected probe energy or (ii) where $\tau$ was shared amongst all the selected probe energies yielded similar values for $\langle \tau \rangle$, but smaller values for $1\sigma$. The error, $\sigma$, for $k_{CS(2)}/k_{CS(1)}$, where $k_{CS} = (\tau_{CS})^{-1}$, was calculated using standard error propagation.

Kinetic analysis at 295 K is complicated by changes in the shape and intensity of the radical pair (RP) ESA, likely due to structural or solvent relaxation following CS that occurs on a similar timescale. Therefore, $k_{CS(2)}/k_{CS(1)}$ was evaluated semi-quantitatively by scaling the time delays $\Delta t$ of the kinetic traces for 1 at the $1^\ast$An ESA by a factor of $q = 1–4.5$ and calculating the sum of the residuals-squared, $\sum \chi^2(\Delta t, q)$, between the 2 and scaled 1 kinetic traces to find the factor $q \approx k_{CS(2)}/k_{CS(1)}$ that best approximates the relative rate of decay of 2 (Figure S9). The curves used for the comparisons were generated by normalizing the kinetic traces from 0 to 1, following the
IRF, and dividing the time-delay axis ($\Delta t$) by $q$. This analysis was repeated for measurements performed on three separate days. This analysis was also performed for data collected in Me-THF at 90 K to demonstrate that it yielded comparable results to the rate ratios determined via fitting the kinetic traces to eq S2.

1.6 Pump pulse and instrument response characterization

Figure 1B in the main text shows a typical pump pulse spectrum, centered at 3.49 eV (355 nm) with 0.075 eV (7.6 nm) full-width at half-maximum (FWHM). The CaF$_2$ prism compressor, used to pre-compensate for accumulated second order dispersion, was optimized by minimizing the duration of the x-corr of the pump and probe monitored by the OKE in a ~100 µm thick glass slide. The OKE experiments were conducted as described above except that the probe pulse polarization was rotated to about $-45^\circ$ relative to the pump and the pump pulse was directed through 1 mm of 1,4-dioxane and 1.2 or 5.5 mm of quartz to account for the dispersion accumulated in the sample and front face of the cuvette (295 K) or front cryostat windows (90 and 5.5 K). The optimum apex-to-apex distance of the prism compressor was determined to be 250 and 300 mm for experiments performed at ambient and cryogenic temperatures, respectively, yielding an OKE signal that fit to ~60 fs (Figure S1). The 3.37 eV (368 nm) excitation pulse used for measurements at the other cryogenic temperatures was optimized and characterized in a similar manner yielding an OKE signal that fit to ~50 fs.
Figure S1. Pump–probe cross correlation monitored by optical Kerr effect. (A) Typical x-corr of the pump (3.49 eV, 500 nJ/pulse) and probe given by the OKE response in an ~100 μm thick glass slide under conditions similar to those in the TA experiments with the (B) time trace and overlaid Gaussian fit at a probe energy of 2.25 eV (550 nm). The non-Gaussian response at probe energies greater than 3 eV resulted from reduced extinction by the analyzing polarizer at those energies.

TA measurements were performed on solutions of anthracene (An) in Me-THF (90 K) following excitation at 3.49 eV (Figure S2) to evaluate $\tau_{IRF}$ in the full experimental set-up. The values of $\tau_{IRF}$ obtained via fitting kinetic traces at various probe energies to eq S2 were larger than the measured 60 fs x-corr, likely due to pump–probe overlap and the resulting cross-phase modulation in the sample and front and back quartz windows of the sample holder (3-3.5 mm total) which stretches the instrument response through group velocity mismatch (GVM), as indicated by the increasing x-corr at probe energies farther from that of the pump. The kinetic trace at a probe energy of 2.05 eV further supports that this response results from pump–probe interactions in the front and back quartz windows since the rise of the An $S_n \leftrightarrow S_1$ excited-state absorption (ESA) (~140 fs) is shorter than the x-corr (>500 fs). To minimize the contribution from GVM, kinetic analysis was performed at probe energies (3.1–3.4 eV) near the excitation pulse where $\tau_{IRF}$ was determined to be ~100 fs (see section 6).
Figure S2. Instrument response function characterization. (A) TA spectra of An in Me-THF at 90 K following excitation at 3.49 eV (300 nJ/pulse) and (B) kinetic traces at select probe energies overlaid with the fit to eq S2.

1.7 Computational details

Density functional theory (DFT) calculations were performed in Q-Chem\textsuperscript{2} at the level of long-range corrected (LRC) LRC-\omega PBEh/6-31G(d)//\omega B97X-D/6-31G(d)\textsuperscript{3,4} in vacuo in recognition of the spurious charge-transfer (CT) states potentially contributing to the electronic structures of the donor-acceptor (D-A) molecules examined here. The stationary ground-state geometries (with no imaginary vibration frequencies found) were first searched at the \omega B97X-D/6-31G(d) (default \omega = 0.2 bohr\textsuperscript{−1}) level of theory without symmetry constraint. Using these optimized geometries, a series of calculations at the LRC-\omega PBEh/6-31G(d) level were performed in order to find the range-separation parameter (\omega) appropriate for each molecule. The optimal \omega was identified for each compound by following Baer’s method\textsuperscript{5} when the value of \(|[E^n(\omega) - E^{n-1}(\omega)] - \varepsilon_{HOMO}(\omega)|\) is minimized, where \([E^n - E^{n-1}]\) is the energy difference between the neutral (n electrons) and the oxidized (n − 1 electrons) states and \(\varepsilon_{HOMO}\) is the HOMO energy of the neutral molecule. Parameters of \omega = 0.164 and 0.164 bohr\textsuperscript{−1} were found for 1 and 2, respectively, and were used in
the calculations for determining the CS internal reorganization energy, $\lambda_i$, for each molecule (vide infra). Normal mode analysis following geometry optimization for all structures yielded no imaginary frequencies.

Long-range correction in the functional can be important for the molecules under study. For instance, we found that the first two singlet excited states of 2 would be predicted erroneously to have a strong CT character with the transition energy of 1.34 and 1.46 eV if computed at the TD-B3LYP/6-31G(d) level. Such a problem is mitigated when the LRC-$\omega$PBEh functional was used; instead, localized triptycene-bis(quinone)-centered transitions at 2.72 and 2.73 eV were found, consistent with the experimental UV-vis spectra for these compounds (Figures 1 and S5).

2. Synthesis and characterization

\[ \text{Figure S3. Synthetic route to 1.} \]
A mixture of 0.51 g of 2-bromoanthracene (2.0 mmol) and 1.08 g of 1,4-benzoquinone (10.0 mmol) in acetic acid (20 mL) was refluxed for 3 h. The reaction mixture was then poured into water, and the precipitate was filtrated and washed with hot water giving 0.49 g of compound 3 (67%). $^1$H NMR (500 MHz, CD$_2$Cl$_2$): $\delta$7.68 (d, $J = 2.0$ Hz, 1H), 7.48-7.40 (m, 2H), 7.31 (d, $J = 7.5$ Hz, 1H), 7.18 (dd, $J = 7.5$ Hz and 2.0 Hz, 1H), 7.09-7.01 (m, 2H), 6.61 (s, 2H), 5.77 (s, 1H), 5.75 (s, 1H). $^{13}$C NMR (125 MHz, CD$_2$Cl$_2$): $\delta$ 183.6, 183.6, 152.0, 151.6, 146.6, 143.7, 143.5, 143.4, 135.8, 128.7, 127.9, 126.1, 126.1, 126.1, 124.9, 124.8, 119.3, 47.4, 47.2. HRMS-ESI$^-$ (m/z) calcd for C$_{20}$H$_{11}$BrO$_2$ (M)$^-$: 361.9948, found: 361.9938.

0.14 g of compound 3 (0.39 mmol) was dissolved in a mixture of AcOH (1 mL) and tetrahydrofuran (1 mL). 0.6 g of Zinc dust was added and the mixture was sonicated at room temperature for 10 min. The zinc dust was removed by filtration and washed with ethyl acetate. The filtrate was collected and the solvent was then removed by rotary evaporation giving compound 4 with a quantitative yield. $^1$H NMR (500 MHz, (CD$_3$)$_2$CO): $\delta$ 7.88 (br, 2H, OH), 7.61 (d, $J = 2.0$ Hz, 1H), 7.47-7.39 (m, 2H), 7.37 (d, $J = 7.5$ Hz, 1H), 7.16 (dd, $J = 7.5$ Hz and 2.0 Hz, 1H), 7.03-6.95 (m, 2H), 6.41 (s, 2H), 5.95 (s, 1H), 5.94 (s, 1H). $^{13}$C NMR (125 MHz, (CD$_3$)$_2$CO):
δ 149.8, 146.6, 146.5, 146.2, 146.2, 133.0, 132.8, 128.3, 127.5, 126.2, 125.9, 125.9, 124.7, 124.6, 118.5, 114.3, 114.2, 47.9, 47.7. HRMS-ESI⁻ (m/z) calcd for C_{20}H_{12}BrO_2 (M-H)^−: 363.0026, found: 363.0026.

36 mg of compound 4 (0.05 mmol), 46 mg of 2-(anthracen-9-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane⁶ (0.15 mmol), and 69 mg of potassium carbonate (0.50 mmol) were combined in 10 mL of tetrahydrofuran and 5 mL of water, and this solution was purged with nitrogen for 15 min. After adding 3 mg of tetrakis(triphenylphosphine)palladium (0.003 mmol) to the solution, the solution was purged with nitrogen for another 15 min. The solution was then heated at 80°C for 12 h. The solution was cooled and then the solvent was removed by rotary evaporation. The product was purified by silica gel column chromatography with dichloromethane/ethyl acetate (9/1) as the mobile phase yielding crude coupling product 5. Then, all the crude product and 100 mg of silver(I) oxide (0.43 mmol) were combined in 5 mL acetone and this solution was heated at 60°C for 3 h. The mixture was washed through a pad of silica gel with dichloromethane and the solvent was then removed by rotary evaporation. The product was purified by silica gel column chromatography with hexanes/ethyl acetate (9/1) as the mobile phase yielding 3 mg of 1. (13% over 2 steps). \(^1\)H NMR (500 MHz, (CD₃)₂CO): δ 8.60 (s, 1H), 8.10 (d, \(J = 8.0\) Hz, 2H), 7.78 (d, \(J = 7.0\) Hz, 1H), 7.63 (d, \(J = 7.0\) Hz, 1H), 7.66-7.39 (m, 6H), 7.34-7.25 (m, 2H), 7.17-7.08 (m, 3H), 6.82-6.73 (m, 2H), 6.06 (s, 1H), 5.98 (s, 1H). \(^{13}\)C NMR (125 MHz, (CD₃)₂CO): δ 184.3, 184.2, 152.8, 152.7, 145.5, 145.1, 145.1, 144.4, 137.2, 136.8, 136.5, 132.3, 131.1, 131.0, 129.3, 129.0,
127.8, 127.6, 127.2, 127.1, 126.5, 126.4, 126.0, 125.4, 125.2, 48.2, 48.1. HRMS-ESI (m/z) calcd for C\textsubscript{34}H\textsubscript{21}O\textsubscript{2} (M+H): 461.1536, found: 461.1534.

Figure S4. Synthetic route to 2.

100 mg of \textit{1,4,5,8-tetrabutoxyanthracene} \textsuperscript{7} (0.21 mmol) in 10 mL of 1,2-dimethoxyethane and 45 mg of isopentyl nitrite (0.38 mmol) were heated to 85 °C. 90 mg of 2-amino-5-bromobenzoic acid (0.42 mmol) in 10 mL of 1,2-dimethoxyethane was added slowly to the solution over 30 min. The mixture was cooled down to room temperature and an additional portion of isopentyl nitrite (0.38 mmol) was added at once. After resuming reflux, another portion of 2-amino-5-bromobenzoic acid (0.42 mmol) in 10 mL of 1,2-dimethoxyethane was added over 30 min. The reaction mixture was cooled to room temperature and 15 mL of 1 M sodium hydroxide was added. The resulting mixture was then transferred to a separatory funnel and extracted three
times with dichloromethane; the combined organic layers were dried over anhydrous sodium sulfate. The solvents were removed under reduced pressure. The crude product was purified by silica gel column chromatography with dichloromethane/hexanes (1/4) giving 20 mg of compound 6 (15% yield). 

$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.51 (d, $J = 2.0$ Hz, 1H), 7.23 (d, $J = 7.5$ Hz, 1H), 7.05 (dd, $J = 7.5$ Hz and 2.0 Hz, 1H), 6.47 (s, 4H), 6.27 (s, 1H), 6.26 (s, 1H), 3.95-3.85 (m, 8H), 1.83-1.73 (m, 8H), 1.63-1.54 (m, 8H), 1.04-0.95 (m, 12H).

$^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 148.7, 148.5, 145.5, 135.7, 135.4, 127.4, 127.0, 125.2, 118.1, 111.0, 110.7, 69.5, 69.4, 40.8, 40.6, 31.7, 31.7, 19.4, 19.4, 14.0, 14.0. HRMS-ESI$^+$ (m/z) calcd for C$_{36}$H$_{46}$BrO$_4$ (M+H)$^+$: 621.2574, found: 621.2571.

31 mg of compound 6 (0.05 mmol), 23 mg of 2-(anthracen-9-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane$^6$ (0.075 mmol), and 53 mg of potassium phosphate tribasic (0.25 mmol) were combined in 15 mL of toluene and this solution was purged with nitrogen for 15 min. After adding 3 mg of tetrakis(triphenylphosphine)palladium (0.003 mmol), the solution was purged with nitrogen for another 15 min. The solution was then heated at 110°C for 12 h. The solution was cooled and then the solvent was removed by rotary evaporation. The product was purified by silica gel column chromatography with dichloromethane/hexanes/triethylamine (24/75/1) as the mobile phase yielding compound 7 (17 mg, 47%). 

$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 8.44 (s, 1H), 8.00 (d, $J = 9.0$ Hz, 2H), 7.65 (d, $J = 9.0$ Hz, 2H), 7.58 (d, $J = 7.5$ Hz, 1H), 7.45 (s, 1H), 7.43-7.39 (m, 2H), 7.28-7.24 (m, 2H), 7.02 (d, $J = 7.5$ Hz, 1H), 6.56 (d, $J = 9.0$ Hz, 2H), 6.54 (d, $J = 9.0$ Hz, 2H), 6.49 (s, 1H), 6.37 (s, 1H), 4.02-3.99 (m, 4H), 3.94-3.90 (m, 4H), 1.91-1.85 (m, 4H), 1.78-1.72 (m, 4H),
1.68-1.62 (m, 4H), 1.54-1.49 (m, 4H), 1.07 (t, J = 7.0 Hz, 6H), 1.92 (t, J = 7.0 Hz, 6H). \(^\text{13}^\text{C}\) NMR (125 MHz, CDCl\(_3\)): δ 148.8, 146.3, 145.4, 137.5, 136.7, 136.4, 134.9, 131.3, 130.3, 128.1, 127.5, 127.4, 126.7, 126.2, 125.0, 125.0, 123.6, 111.0, 110.6, 69.7, 69.4, 41.3, 41.0, 31.8, 31.7, 19.5, 19.3, 14.1, 13.9. HRMS-ESI\(^+\) (m/z) calcd for C\(_{50}\)H\(_{55}\)O\(_4\) (M+H)\(^+\): 719.4095, found: 719.4085.

To a solution of 12 mg of compound 7 (0.05 mmol) in 5 mL of dichloromethane was added 0.2 mL of 1 M boron tribromide in dichloromethane at 0 °C under nitrogen. The mixture was slowly warmed to the ambient temperature and stirred for 12 h. The resulting material was extracted with ethyl acetate and water, and the combined organic layers were dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure giving crude product 8. Then, 10 mg of crude product 8 and 56 mg of silver(I) oxide (0.24 mmol) were combined in 5 mL acetone and the solution was heated at 60°C for 3 h. The mixture was washed through a pad of silica gel with dichloromethane giving 10 mg of 2 (41% over 2 steps). \(^1^\text{H}\) NMR (500 MHz, CDCl\(_3\)): δ 8.49 (s, 1H), 8.03 (d, J = 8.0 Hz, 2H), 7.67 (d, J = 7.5 Hz, 1H), 7.55 (d, J = 2 Hz, 1H), 7.50 (d, J = 8.0 Hz, 2H), 7.45-7.42 (m, 2H), 7.32-7.28 (m, 2H), 7.13 (dd, J = 7.5 Hz and 2.0 Hz, 1H), 6.76-6.67 (m, 4H), 6.28 (s, 1H), 6.17 (s, 1H). \(^\text{13}^\text{C}\) NMR (125 MHz, CDCl\(_3\)): δ 182.3, 182.2, 151.9, 151.7, 136.6, 136.5, 131.3, 130.2, 129.0, 128.5, 128.3, 127.1, 126.4, 125.6, 125.1, 42.3, 42.2. HRMS-APPI\(^+\) (m/z) calcd for C\(_{34}\)H\(_{19}\)O\(_4\) (M+H)\(^+\): 492.1278, found: 492.1292.
3. Additional steady-state optical spectroscopy

Figure S5 provides reference absorption spectra for An and triptycene-mono(benzoquinone) (tBQ). The absorption centered at ~3 eV for tBQ likely results from n \rightarrow \pi^* transitions localized on the BQ moiety, as was previously reported for related compounds, and is also observed at < 3 eV in the absorption spectra of 1 and 2 (Figure 1B). This absorption is weaker than that due to the 1^*An \leftrightarrow S_0 transition by a factor of \geq 10, and therefore likely has negligible contribution to the observed photophysics.

![Figure S5](image.png)

**Figure S5.** Steady-state absorption spectra. (A) Reference compounds and (B) normalized steady-state absorption spectra obtained in THF at 295 K.

4. Additional time-resolved optical spectroscopy

TA spectra of An and tBQ in Me-THF at 90 K are presented in Figure S6 for comparison. Excitation of An at 3.49 eV yields 1^*An as indicated by the characteristic ESA at 2.05 and 3.32 eV, ground-state bleach (GSB) at 3.25 and 3.64 eV, and stimulated emission (SE) at 2.73, 2.90, 3.08, and 3.25 eV. The ESA and SE decay on the nanosecond timescale to yield new ESA (2.89, 3.05 eV) showing intersystem crossing from 1^*An to 3^*An. 3^*An decays on a timescale much longer than the temporal range of the experiment (~6 ns). Excitation of tBQ at 3.49 eV yields weak ESA centered at ~3.4 eV which decays to new ESA centered at ~2.7 eV within 25 ps. The terminal state
then decays on a timescale much longer than the temporal window of the experiment. Additionally, the low intensity of the tBQ ESA features indicates that parasitic co-excitation of the tBQ moieties in 1 and 2 contribute negligibly to the observed TA spectra. This is a result of the extinction coefficient of anthracene being about 44x larger than triptycene with one BQ and 22x larger than triptycene with two BQs at 355 nm.¹⁰

TA spectra at short time delays for solutions of 1 and 2 in Me-THF at 5.5 K are presented in Figure S7. TA spectra at long time delays are available from the corresponding authors upon request.

![Figure S6](image)

**Figure S6.** TA spectra of reference compounds. TA spectra following excitation at 3.49 eV (200–300 nJ/pulse, <50 fs) of (A) An and (B) tBQ in Me-THF at 90 K.
Figure S7. 5.5 K TA Spectra. TA spectra following excitation at 3.49 eV (200–400 nJ/pulse, <50 fs) of (A) 1 and (B) 2 in Me-THF at 5.5 K.

5. Electrochemistry and electron transfer energetics

Figure S8 shows that the 1,4-benzoquinone (BQ) reduction potential splits in 2, indicating electronic interaction between the two BQ moieties. This results in a less negative reduction potential ($E^-$) for 2 compared to 1. This change in $E^-$ is partially offset by a more positive oxidation potential ($E^+$) for 2 compared to 1, likely due to the presence of a second electron-withdrawing BQ moiety. The combination of these changes to $E^-$ and $E^+$ result in modest decreases in $E^+ - E^-$ for 2 of 70 mV compared to 1. The one-electron redox potentials of 1 and 2 in THF are summarized in Table S1.
The free energy change, $\Delta G_{CS}$, associated with CS were estimated for each compound using eq S3,

$$\Delta G_{CS} = -E_{00} + e\left(E^+ - E^-\right) - \frac{e^2}{R_{DA}\varepsilon} + \frac{e^2}{\varepsilon}\left(\frac{1}{2r_+} + \frac{1}{2r_-}\right)\left(\frac{1}{\varepsilon} - \frac{1}{\varepsilon'}\right)$$  \hspace{1cm} \text{(S3)}

where $E^+$ and $E^-$ are the An oxidation and BQ reduction potentials, respectively, $e$ is the charge of the electron, $\varepsilon$ is the static dielectric constant of the medium in which the measurement is made, $\varepsilon'$ is the static dielectric constant of the solvent in which $E^+$ and $E^-$ are determined, $r_+$ is the radius of An$^{++}$, $r_-$ is the radius of BQ$^{+}$, and $R_{DA}$ is the An$^{++}$-BQ$^{+}$ distance. The value of $R_{DA}$ was obtained from the DFT geometry-optimized structures, while the values of $r_+$ and $r_-$ were assumed to each be $R_{DA}/2$ as has been suggested for closely-spaced D-A systems.\textsuperscript{12} The average of the energies of the An 0-0 vibronic absorption band and the $1^*\text{An}$ 0–0 vibronic fluorescence emission bands were used to determine the $1^*\text{An}$ energy, where $E_{00} = 3.16$ eV for both 1 and 2. The room temperature

\textbf{Figure S8.} Cyclic voltammetry of solutions of 1 and 2 in THF.
electrochemistry was performed in THF ($\varepsilon' = 7.52$). For glassy Me-THF, $\varepsilon' = 2.6$. Energetic parameters are given in Table S1.

### Table S1. Energetic Parameters.

<table>
<thead>
<tr>
<th></th>
<th>$E^+$ (V)$^a$</th>
<th>$E^-$ (V)$^a$</th>
<th>$R_{DA}$ (Å)$^b$</th>
<th>$\lambda$ (eV)</th>
<th>$\Delta G_{CS}$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>295 K</td>
<td>90 K</td>
<td>295 K</td>
<td>90 K</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>1.28</td>
<td>-0.48</td>
<td>8.39</td>
<td>0.48</td>
<td>0.40</td>
</tr>
<tr>
<td>2</td>
<td>1.30</td>
<td>-0.39</td>
<td>7.98</td>
<td>0.38</td>
<td>0.30</td>
</tr>
</tbody>
</table>

$^a$ V vs saturated calomel electrode (SCE).

$^b$ For 2, $R_{DA}$ assumes the charge distribution is centered between the two BQs.

The total nuclear reorganization energy for the CS reaction is given by $\lambda = \lambda_s + \lambda_i$, where $\lambda_s$ accounts for nuclear reorganization the solvent and $\lambda_i$ accounts for nuclear reorganization of the donor and acceptor. Values for $\lambda_i$ were estimated using eq S4–S5 where $\lambda^+/−_i$ is the $\lambda_i$ associated with the radical cation/anion, $E_{opt}^+/−$ is the energy of the radical ion at the optimized geometry, and $E_{neutral}^+/−$ is the energy of the radical ion at the optimized geometry of the neutral compound. The energies determined from the DFT calculations are provided in Table S2.

$$\lambda_i = \lambda^+_i + \lambda^-_i$$  \hspace{1cm} (S4)

$$\lambda^+/−_i = E_{neutral}^+/− - E_{opt}^+/−$$  \hspace{1cm} (S5)

The solvent reorganization energy was estimated using eq S6 for room temperature solutions and is assumed to be $\lambda_s = 0$ in frozen glassy solvents.$^{15}$

$$\lambda_s = \frac{e^2}{\varepsilon} \left( \frac{1}{2r^+} + \frac{1}{2r^-} - \frac{1}{R_{DA}} \right) \left( \frac{1}{n^2} - \frac{1}{\varepsilon^2} \right)$$  \hspace{1cm} (S6)

In eq S6, $n$ is the refractive index and in 1,4-dioxane $n = 1.42$ and $\varepsilon = 2.22$.}$^{13}$
Table S2. Energies of geometry-optimized structures and single point calculations.

<table>
<thead>
<tr>
<th></th>
<th>$E_{\text{neutral}}$ (hartree)</th>
<th>$E_{+\text{neutral}}$ (hartree)</th>
<th>$E_{-\text{neutral}}$ (hartree)</th>
<th>$E_{+\text{opt}}$ (hartree)</th>
<th>$E_{-\text{opt}}$ (hartree)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-1456.58902060559</td>
<td>-1456.33736554</td>
<td>-1456.65139291</td>
<td>-1456.34247942623</td>
<td>-1456.66110634200</td>
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<tr>
<td>2</td>
<td>-1605.65142381331</td>
<td>-1605.39603045</td>
<td>-1605.72597364</td>
<td>-1605.40163608565</td>
<td>-1605.73134467554</td>
</tr>
</tbody>
</table>

6. Kinetic analysis

Figure S9 shows the sum of the residuals squared between kinetic traces for 1 scaled by a factor $q$ and kinetic traces for 2 at 295 and 90 K. This analysis was completed using kinetic traces at probe energies of 3.30 eV (295 K measurements) and 3.28 eV (90 K measurements) from experiments performed on three separate days.

Figure S9. Sum of the residuals-squared between the single-acceptor kinetic trace with $\Delta t/q$ and the two-acceptor kinetic trace for 1 and 2. Shading above and below represents ± 1σ based on experiments performed on three days.

Kinetic traces at select probe energies spanning the $1^\text{st} \text{An} \text{ESA}$ at ~3.2 eV for the first 10 ps were fit using eq S2 for 1 and 2 in Me-THF at cryogenic temperatures. Example kinetic traces and fits for samples at 90 and 5.5 K are given in Figure S10 and the resultant $\tau_s$ and IRFs are given in Table S3. Each panel shows kinetic traces from one individual scan with 0.5 s averaging per time
delay. At 5.5 K, the ratio $[k_{CS}(2)/k_{CS}(1)] \pm \sigma$, where $\sigma$ is the standard deviation, was determined to be $5.0 \pm 0.8$ and is represented in Figure S11 where example kinetic traces are overlaid with simulated decay kinetics obtained from $2 \times k_{CS}(1)$ and $4 \times k_{CS}(1)$. The progressively lighter shading around the measured kinetic data illustrates up to $3\sigma$ of $<k_{CS}>$.

**Figure S10.** Sample Kinetic Fits at 90 and 5.5 K. Kinetic traces at select probe energies overlaid with fits to eq S2, to demonstrate the quality of the obtained fits, for 1 in Me-THF at (A) 90 and (B) 5.5 K, 2 in Me-THF at (C) 90 and (D) 5.5 K.

**Table S3.** Fit parameters for 1 and 2. Resultant time constants (fs), with the IRF given in parentheses, for the fits shown in Figure S10.

<table>
<thead>
<tr>
<th></th>
<th>3.38 eV (367 nm)</th>
<th>3.36 eV (370 nm)</th>
<th>3.32 eV (373 nm)</th>
<th>3.30 eV (375 nm)</th>
<th>3.28 eV (378 nm)</th>
<th>3.26 eV (380 nm)</th>
<th>3.24 eV (383 nm)</th>
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<tbody>
<tr>
<td><strong>1</strong> (90 K)</td>
<td>1065 (102)</td>
<td>1060 (101)</td>
<td>1082 (98)</td>
<td>1162 (96)</td>
<td>1257 (95)</td>
<td>1310 (94)</td>
<td>1425 (89)</td>
</tr>
<tr>
<td><strong>2</strong> (90 K)</td>
<td>295 (92)</td>
<td>251 (98)</td>
<td>223 (102)</td>
<td>263 (100)</td>
<td>269 (98)</td>
<td>285 (94)</td>
<td>287 (87)</td>
</tr>
<tr>
<td><strong>1</strong> (5.5 K)</td>
<td>---</td>
<td>1371 (97)</td>
<td>1503 (96)</td>
<td>1612 (94)</td>
<td>1669 (97)</td>
<td>1678 (94)</td>
<td>1771 (89)</td>
</tr>
<tr>
<td><strong>2</strong> (5.5 K)</td>
<td>308 (95)</td>
<td>291 (98)</td>
<td>276 (94)</td>
<td>301 (93)</td>
<td>325 (93)</td>
<td>339 (90)</td>
<td>323 (88)</td>
</tr>
</tbody>
</table>
Figure S11. Kinetic comparison at 5.5 K. Kinetic traces normalized from 0 to 1 for 1 and 2 in Me-THF, 5.5 K, probe energy = 3.28 eV. The progressively lighter gray and blue shadings in depict the standard deviations of the average rate constant, $k_{CS}(1) \times 2$ and $k_{CS}(1) \times 4$.

7. Theory background

A simple Hamiltonian $H$ for describing the donor $D$ ($^1$An) with energy $E_D$ coupled to two acceptors (RP states) $RP_1$, $RP_2$ with energy $E_{RP}$ and the donor-acceptor coupling constant $V_{DA}$ is given in eq S7-S8

$$H = E_D c_D^\dagger c_D + E_{RP} c_{RP_1}^\dagger c_{RP_1} + E_{RP} c_{RP_2}^\dagger c_{RP_2} + H_V$$

(S7)

$$H_V = V_{DAC_D} c_{RP_1} + V_{DAC_D} c_{RP_2} + H.c.$$  

(S8)

where $c^\dagger$, $c$ are electron creation/annihilation operators and $H.c.$ is the Hermitian conjugate. Equivalently, one can write the coupling term as in eq S9-S10

$$H_V = \sqrt{2} V_{DAC_D} c_{RP_+} + H.c.$$  

(S9)

$$c_{RP_+} = (c_{RP_1} + c_{RP_2})/\sqrt{2}$$

(S10)

where only the superposition bonding state $RP_+$ of the two acceptors is coupled to the donor. When the two acceptors are coupled to each other with $V'$ there will be an energy gap between the bonding
RP⁺ and anti-bonding RP⁻ states, but the donor still couples to only RP⁺ with normalized coupling \( \sqrt{2} V_{DA} \).

What differentiates between these two representations is the way the bath is coupled to the quantum system. At high temperatures or when the two acceptors are far from each other, the bath is coupled to each of them independently and the energy fluctuations of RP₁ and RP₂ are uncorrelated. This is equivalent to coupling the two acceptors to independent baths and represents the statistical or incoherent limit where the CS rate constant with two acceptors \( k_{CS}(2) \) is twice that of the CS rate constant with one acceptor \( k_{CS}(1) \), \( k_{CS}(2)/k_{CS}(1) = 2 \). On the other hand, if the bath is coupled to the acceptors coherently through the RP⁺ state, \( k_{CS}(2)/k_{CS}(1) \) can be greater than 2 due to quantum coherence as shown below.

We use the spin-boson model\(^{16,17} \) to describe the dynamics of the system and the effect of quantum coherence on \( k_{CS} \). In this model, the general donor-acceptor quantum system is represented by a two-level system characterized by the donor-acceptor energy difference \( \Delta G_{CS} \) and coupling \( V_{DA} \). The environment is a bosonic bath of harmonic oscillators each with mass \( m_i \) and frequency \( \omega_i \). The bath frequencies have a normal distribution around the bath characteristic frequency \( \omega_c = 1/\tau_c \) where \( \tau_c \) is the bath relaxation time.

The bath can be coupled to local energy levels of the acceptor or donor and/or to the coupling \( V \) depending on the system and the nature of the interaction between the system and the bath.\(^{17} \) In the former model, the system-bath Hamiltonian \( H_{SB} \) is given in eq S11

\[
H_{SB} = \sum_i g_i x_i \rho_A \quad (S11)
\]

\[
g_i = V_{SB} \sqrt{(2m_i \omega_i)/\hbar} \quad (S12)
\]

where \( g_i \) is the system-bath coupling defined in eq S12, \( x_i \) is the displacement of the harmonic mode \( i \) when the charge is moved to the acceptor (\( \rho_A = 1 \)). The coupling between each mode of the
bath and the system is $V_{SB}$, which determines the spectral function and the reorganization energy of the bath. The spectral function of the bath $J(E)$ is defined in eq S13.

$$J(E) = \pi \hbar \sum_i \frac{g_i^2}{2m_i \omega_i} \delta(E - \hbar \omega_i)$$  \hspace{1cm} (S13)

This function describes the frequency distribution of the bath and the strength of system-bath coupling. The reorganization energy of the bath $\lambda_B$ is defined in eq S14.

$$\lambda_B = \frac{1}{\pi} \int_0^\infty J(E) dE$$  \hspace{1cm} (S14)

$\lambda_B$ measures the energy required for the bath harmonic modes to adjust to themselves when the charge is transferred to the acceptor according to $H_{SB}$ (eq S11).

For a dynamical bath with short relaxation time $\tau_c E \ll 1$ and in the weak system-bath coupling regime, the CS rate constant is given approximately by eq S15-S16 where $E^2 = \Delta G_{CS}^2 + V_{DA}^2$.

$$k_{CS} \approx \left( V_{DA}^2 \kappa \right) / (\kappa^2 + \Delta G_{CS}^2)$$  \hspace{1cm} (S15)

$$\kappa(E) = \frac{J(E)}{2} \coth \left( \frac{E}{2k_B T} \right)$$  \hspace{1cm} (S16)

At low temperatures $\kappa \ll E$, $V_{DA}$ and high driving force $\Delta G_{CS} > V_{DA}$ the charge oscillates between the donor and the acceptor with the frequency of $V_{DA}$ and at the same time tunnels from the donor to the acceptor with $k_{CS}$ given approximately in eq S17.

$$k_{CS} \approx \left( V_{DA}^2 \kappa \right) / \Delta G_{DA}^2$$  \hspace{1cm} (S17)

In the single-acceptor case, the donor couples to the acceptor with $V_{DA}$ and the acceptor couples to each mode of the bath with $V_{SB}$, such that $k_{CS}(1) \propto V_{DA}^2 \kappa$. In the incoherent two-acceptor case, the donor couples independently to each acceptor with $V_{DA}$ and each acceptor couples independently to each mode of the bath with $V_{SB}$, such that $k_{CS}(2) = k_{CS}(RP_1) + k_{CS}(RP_2)$. If $k_{CS}(RP_1) = k_{CS}(RP_2) \propto V_{DA}^2 \kappa$, then $k_{CS}(2) \propto 2V_{DA}^2 \kappa$, i.e. $k_{CS}(2) = 2 \times k_{CS}(1)$. In the coherent two-
acceptor model, the donor couples to the bonding superposition state $RP_+$ with $\sqrt{2}V_{DA}$ and $RP_+$ couples to each mode of the bath with $\sqrt{2}V_{SB}$.

Renormalization of $V_{DA}$ and $V_{SB}$ replaces $V_{DA}$ and $\kappa$ in eq S17 with $2V_{DA}^2$ and $2\kappa$, which gives $k_{CS}(2) \propto 4V_{DA}^2\kappa$, i.e. $k_{CS}(2) = 4 \times k_{CS}(1)$. Thus, the coherent two-acceptor case leads to a factor of two increase in $k_{CS}$ compared to the incoherent two-acceptor case and a factor of four increase in $k_{CS}$ compared to the single-acceptor case.

As we increase the temperature, $k_{CS}$ shows a turn-over behavior and starts to decrease, though we expect that rather than observe the high temperature coherent regime, upon raising the temperature the dynamics will transition from the coherent model to the incoherent model as increased thermal energy transitions the system from correlated fluctuations in the acceptors energies and structures to uncorrelated fluctuations.

8. References


