Supporting Information

for

Quantum Coherence in Ultrafast Photo-driven Charge Separation

Authors:

Brian T. Phelan¹, Jonathan D. Schultz¹, Jinyuan Zhang, Guan-Jhih Huang, Ryan M. Young^{*},

Michael R. Wasielewski*

^vBrian T. Phelan and Jonathan D. Schultz contributed equally

*Correspondence to: <u>m-wasielewski@northwestern.edu</u>, <u>ryan.young@northwestern.edu</u>

Affiliations:

Department of Chemistry and Institute for Sustainability and Energy at Northwestern, Northwestern University, Evanston, IL 60208-3113, USA

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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. MALDI-MS spectra were measured on a Bruker Autoflex III MALDI-TOF using 2-hydroxy-1-naphthoic acid as the matrix. LC-TOF ESI and APPI spectra were measured on Agilent 6210A. High resolution mass spectra (HRMS) were obtained with an Agilent LCTOF 6200 series mass spectrometer using electrospray ionization (ESI) and APPI.

1.2 Time-resolved optical spectroscopy

In addition to the transient absorption (TA) experimental details provided in the main text, the pump pulse was directed through a mechanical chopper (500 Hz) and focused to a diameter (1/e definition) of about 250 μ m (room temperature measurements) or about 500 μ m (cryogenic temperature measurements) at the sample using a 500 mm focal length lens. The CaF₂ crystal used for continuum generation was translated 7.5 mm at 1.15 mm/s to avoid damaging the crystal using the X-MCB1/LAC10A-T4 controller/linear actuator pair (Zaber Technologies Inc). TA spectra were collected by averaging for a total of 1-3 s per time delay and 0.5 s per time delay per scan of the delay stage. The reported Δ A signals were calculated by averaging the shot-to-shot difference spectra as shown in Equation S1, where *S*(λ ,*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 pump

light and group delay dispersion were corrected for using Surface Xplorer (Ultrafast Systems, LLC).

$$S(\lambda,t) = \left(-\log_{10} \left(\frac{T_{sig}^*/T_{Ref}^*}{T_{Sig}/T_{Ref}} \right) \right)$$
 Equation S1

1.3 Pump pulse and instrument response characterization



Figure S1. A typical pump pulse spectrum. Fitting to a single Gaussian yields a FWHM of 0.053 eV.

A sample pump pulse spectrum is provided in Figure S1 with the 7 nm full-width at halfmaximum (FWHM) bandwidth indicating a transform-limited minimum duration of about 40 fs. The LaK21 prism compressor separation was optimized by measuring the cross-phase modulation between the pump and probe in a thin (about 100 μ m) glass disk (Figure S2). The signal *S*(*t*) was fit to the sum of a Gaussian and its first two derivatives (Equation S2) each sharing the same timezero *t*₀ and width *w* parameters but with independent amplitudes *B_i* and initial offset *S*₀.

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

The width of the Gaussian instrument response function (IRF) τ_{IRF} was given by the FWHM of the Gaussian IRF, $2w\sqrt{\ln 2}$, and the minimum was found to be about 50 fs (Figure S2B). The IRF showed a strong wavelength dependence in the cuvettes and sample cell, likely due to interaction with the front and back windows stretching the IRF through group velocity mismatch, as indicated by the increasing IRF at probe wavelengths farther from those of the pump (Figure S2A). Nonetheless, fits to kinetic traces at probe wavelengths near that of the pump using Equation S3 indicate τ_{IRF} values less than 100 fs, even for experiments performed using the cryostat. Equation S3 is similar to Equation S2, but it convolutes the Gaussian IRF with the sum of a step function (S_0 before t_0 and S_0' after t_0) and an exponential decay with amplitude A and decay constant τ .

$$S(t) = e^{-\frac{t^2}{w^2}} * \begin{cases} S_0 \\ S_0 + \sum_{i=0}^2 B_i \frac{d^i}{dt^i} [\delta(t-t_0)] + Ae^{-\frac{(t-t_0)}{\tau}} & t < t_0 \\ t \ge t_0 \end{cases}$$
 Equation S3



Figure S2. Pump-probe cross correlation signal (A) at all wavelengths of interest and (B) at a representative probe wavelength of 475 nm. Measurements were conducted using a $\sim 100 \,\mu$ m thick glass disk under conditions similar to those in the fsTA experiments. The fit shown in (B) follows the form of Equation S2 and output an IRF of 52 fs.

In addition to the compounds of interest to this study, fsTA spectra were collected for neat 1,4-dioxane in a 1 mm quartz cuvette to characterize the pump pulse duration using oscillatory signals from impulsively excited vibrational modes.¹ Clear oscillations can be seen in the 1,4-dioxane fsTA spectra in Figure S3A. Fast Fourier transform analysis following truncation of the data at time delays less than 200 fs at $\lambda_{\text{probe}} = 455$ nm yields the power spectrum provided in Figure S3B. Our observation of impulsive excitation of the 836 cm⁻¹ vibrational mode of 1,4-dioxane implies a pump pulse duration of about 40 fs, though the decreased relative intensity of the 836 cm⁻¹ mode suggests the pump pulse duration may actually be slightly longer than 40 fs.



Figure S3. (A) Chirp-corrected fsTA spectra of neat 1,4-dioxane at 295 K illustrating impulsive stimulated Raman scattering following excitation at 2.85 eV (500 nJ/pulse) and (B) a power spectrum of the time-domain oscillations at the probe wavelength of 455 nm. The time-domain oscillation was truncated prior to 200 fs to remove influence from the cross-phase modulation and was subsequently windowed with a Hanning function and zero-padded to give a vector length of 2^{10} .

1.4 Kinetic analysis

Analysis of the charge separation (CS) and room temperature charge recombination (CR) kinetics was performed using Origin 2015 (OriginLab Corporation) by globally fitting kinetic traces at select probe wavelengths spanning the **NDI**^{•-} excited state absorption (ESA) centered at

475 nm to Equation S4, which is a sum of exponential decays with amplitudes A_{j} , decay constants τ_{i} , and offset S_0 .

$$S(t) = S_0 + \sum_j A_j e^{-\frac{(t-t_0)}{\tau_j}}$$
Equation S4

Note that only τ_j was fit globally, all other parameters were fit independently for each selected wavelength. Equation S4 neglects the IRF due to complex lineshapes, though this is expected to have a negligible impact on the determination of τ_{CS} since the observed values of $\tau_{CS} > 2 \ge \tau_{IRF}$. All fitting procedures were conducted using the minimum number of exponentials required to fit the data. In the room temperature fits, two additional exponential decays were included to account for a structural relaxation ($\tau \sim 2$ to 3 ps), and the low-amplitude, long-lived ($\tau \sim 150$ ps) absorption component described in the main text. Figure S4 provides example fits from this analysis for both compounds at each of the temperatures studied here.

The low temperature CR kinetics were analyzed using laboratory-written software in MATLAB (The MathWorks Inc) by globally fitting select probe wavelengths at the **NDI** ground state bleach (GSB) and **NDI**⁻⁻ and **DMA**⁺⁺ ESA to the solution to a sequential first-order kinetic model convoluted with a Gaussian IRF (τ_{IRF}). First, MATLAB numerically solved the differential equations associated with the sequential first order kinetic model (Equation S5) using matrix methods² and convoluted the solution with a Gaussian IRF. Note that a wavelength independent t_0 and τ_{IRF} are implicit in this analysis using MATLAB. Next, MATLAB employed least-squares fitting using the Levenberg-Marquardt method to find the t_0 , A_j , and τ_j that best matched the fit to the raw data. MATLAB then constructs time-dependent population curves for the species in the kinetic model by substituting the optimized parameters into the differential equations and deconvolutes the full two-dimensional raw spectra with the population curves to extract evolution-

associated spectra (EAS) for each species in the kinetic model. Given the wavelength independent t_0 and τ_{IRF} , a fast decay $k_{XPM} = (100 \text{ fs})^{-1}$ was used to approximate the cross-phase modulation and τ_{CS} was fixed to the value obtained using the analysis described above.

$$\begin{bmatrix} -k_{XPM} & 0 & 0 & 0 \\ 0 & -k_{A \to B} & 0 & 0 \\ 0 & k_{A \to B} & -k_{B \to C} & 0 \\ 0 & 0 & k_{B \to C} & 0 \end{bmatrix}; [1, 1, 0, 0]$$
 Equation S5



Figure S4. Kinetic traces at select probe energies overlaid with fits to Equation S4 for (A) **1NDI** and (B) **2NDI** in 1,4-dioxane at 295 K, (C) **1NDI** and (D) **2NDI** in glassy Me-THF at 90 K, and (E) **1NDI** and (F) **2NDI** in glassy Me-THF at 5.5 K. Red lines illustrate fits to Equation S4. The data were not chirp-corrected for this analysis.

1.5 Additional computational details

As mentioned in the main text, occasional imaginary frequencies were output from the normal mode analyses for **1NDI** and **2NDI**. These frequencies are listed in Table S1. Considering the low frequencies of these modes and the tight convergence criterion we restricted the calculations to, we do not expect the presence of these modes to affect the estimation of λ_{v} significantly.

Table S1. Imaginary frequencies from the outputs of normal mode analyses conducted on each species of **1NDI** and **2NDI**.

	Charge	Imaginary Frequencies (cm ⁻¹)
	0	25.43i
1NDI	-1	39.34i
	+1	not converged
	0	-
2NDI	-1	not converged
	+1	-

2. Synthesis and characterization



Scheme S1. Synthetic route to 2NDI and 1NDI



An-2NDI and An-NDI-NH₂: 100 mg (0.26 mmol) of N-octyl-perylene-3,4,9,10tetracarboxylic-3,4-anhydride-9,10-imide³ and 260 mg (0.12 mmol) of 1,8-diaminoanthracene⁴ were stirred under nitrogen in 10 mL of DMF for 16 h at 130 °C. Upon cooling to room temperature, the reaction mixture was diluted with 100 mL of DCM and washed with 100 mL of water and 100 mL of brine. The organic layer was dried over anhydrous Na₂SO₄. The solvents were removed under reduced pressure. The crude product was purified by silica gel column chromatography with DCM/EtOAc (95/5) giving An-2NDI (13 mg, 12 %) and An-NDI-NH₂ (20 mg, 29 %) as two separated products. For An-2NDI: ¹H NMR (500 MHz, CDCl₃): δ 8.70 (s, 1 H), 8.31-8.44 (m, 8 H), 8.20 (d, 2 H, J = 9.0 Hz), 7.58-7.66 (m, 3 H), 7.48 (d, 2 H, J = 9.0 Hz), 4.19-4.31 (m, 4 H), 1.69-1.80 (m, 4 H), 1.18-1.49 (m, 20 H), 0.88 (t, 6 H, J = 7.0 Hz). ¹³C NMR (125 MHz, CDCl₃): δ 162.2, 162.1, 132.7, 131.4, 130.8, 130.3, 130.1, 128.6, 127.8, 127.4, 126.5, 126.2, 126.0, 125.7, 125.3, 114.6, 41.2, 31.9, 29.3, 29.3, 28.0, 27.2, 22.7, 14.1. MALDI-TOF MS (*m/z*): calcd for C₅₈H₄₉N₄O₈^{-:} 929.356; found: *m*/*z* 929.359 ([M-H]⁻). For An-NDI-NH₂: 1H NMR (500 MHz, CD_2Cl_2): δ 8.80-8.86 (m, 4 H), 8.57 (s, 1 H), 8.20 (d, 2 H, J = 8.5 Hz), 8.12 (s, 1 H), 7.64 (dd, 1 H, J = 8.5 Hz and 7.0 Hz), 7.53 (d, 1 H, J = 8.5 Hz), 7.49 (d, 1 H, J = 7.0 Hz), 7.31 (dd, 1 Hz)H, J = 8.5 Hz and 7.0 Hz), 6.72 (d, 1 H, J = 7.0 Hz), 4.18-4.26 (m, 2 H), 4.02-4.13 (br, 2 H), 1.71-1.82 (m, 2 H), 1.23-1.48 (m, 10 H), 0.90 (t, 6 H, J = 7.0 Hz). ¹³C NMR (125 MHz, CD₂Cl₂): δ

163.6, 163.2, 142.5, 133.3, 132.8, 132.6, 131.9, 131.3, 130.3, 128.4, 127.9, 127.7, 127.4, 127.1,
127.0, 126.8, 125.2, 124.8, 119.3, 113.9, 108.7, 41.4, 32.2, 29.7, 29.6, 28.5, 27.5, 23.1, 14.3.
MALDI-TOF MS (*m*/*z*): calcd for C₃₆H₃₁N₃O₄⁺: 569.231; found: *m*/*z* 569.238 ([M]⁺).



Br-An-2NDI: 68 mg of **An-2NDI** (0.073 mmol) was suspended in 30 ml of chlorobenzene and 30 mL of acetic acid. To this solution, 116 mg of bromine (0.73 mmol) was added dropwise. The reaction mixture was stirred in the dark at 50°C for 12 h. After completion of the reaction, the resulting material was extracted with DCM and aqueous sodium thiosulfate solution and combined organic layers were washed with water and dried over anhydrous Na2SO4. The solvents were removed under reduced pressure. The crude product was purified by silica gel column chromatography with DCM/EtOAc (95/5) giving **Br-An-2NDI** (180 mg, 77%). ¹H NMR (500 MHz, CDCl₃): δ 8.71 (d, 2 H, *J* = 9.0 Hz), 8.41(d, 4 H, *J* = 7.5 Hz), 8.33(d, 4 H, *J* = 7.5 Hz), 7.74 (dd, 2 H, *J* = 9.0 Hz and 7.0 Hz), 7.67 (s, 1 H), 7.51 (d, 2 H, *J* = 7.0 Hz), 4.20-4.28 (m, 4 H), 1.66-1.81 (m, 4 H), 1.16-1.49 (m, 20 H), 0.88 (t, 6 H, *J* = 6.5 Hz). ¹³C NMR (125 MHz, CDCl₃): δ 162.1, 162.0, 131.7, 131.6, 130.8, 130.2, 129.9, 128.2, 127.7, 126.9, 126.6, 126.2, 125.9, 125.5, 124.9, 114.8, 41.2, 31.8, 29.7, 29.3, 29.3, 28.0, 27.2, 22.7, 14.1. MALDI-TOF MS (*m/z*): calcd for C₅₈H₄₉BrN₄O₈Na⁺: 1031.263; found: *m/z* 1031.262 ([M+Na]⁺).



2NDI: 35 mg of **Br-An-2NDI** (0.035 mmol), 7 mg of 4-(dimethylamino)phenylboronic acid (0.053 mmol), and 32 mg of potassium phosphate tribasic (0.15 mmol) were combined in 5 mL THF and this solution was purged with nitrogen for 15 min. After adding 3 mg of tetrakis(triphenylphosphine)palladium(0) (0.003 mmol) to the solution, the solution was purged with nitrogen for another 15 min. The solution was then heated at 70°C for 12 h. The solution was cooled and then the solvent was then removed by rotary evaporation. The product was purified by silica gel column chromatography with dichloromethane/ethyl acetate (98/2) as the mobile phase yielding **2NDI** (14 mg, 38%). ¹H NMR (500 MHz, CDCl₃): δ 8.43(d, 4 H, *J* = 7.5 Hz), 8.33(d, 4 H, *J* = 7.5 Hz), 8.00 (d, 2 H, *J* = 8.0 Hz), 7.66 (s, 1 H), 7.43-7.49 (m, 4 H), 7.40 (d, 2 H, *J* = 8.5 Hz), 6.98 (d, 2 H, *J* = 8.5 Hz), 4.21-4.30 (m, 4 H), 3.13 (s, 6H), 1.66-1.81 (m, 4 H), 1.06-1.49 (m, 20 H), 0.88 (t, 6 H, *J* = 6.0 Hz). ¹³C NMR (125 MHz, CD₂Cl₂): δ 162.9, 162.5, 150.8, 141.3, 132.4, 132.1, 132.0, 131.2, 130.7, 129.7, 127.9, 127.4, 127.0, 126.6, 126.4, 126.1, 125.2, 125.1, 113.8, 112.6, 41.5, 40.8, 32.3, 30.1, 29.8, 28.3, 27.6, 23.1, 14.3. MALDI-TOF MS (*m*/*z*): calcd for C₆₆H₅₈N₅O₈: 1048.434; found: *m*/*z* 1048.429 ([M-H]⁻).



An-1NDI: 35 mg (0.06 mmol) of **An-NDI-NH**₂ and 100 mg (0.64 mmol) of cyclohexanedicarboxylic anhydride (predominantly *cis*) were stirred under nitrogen in 20 mL of pyridine for 12 h at 120 °C. Upon cooling to room temperature, the solvent was removed under reduced pressure. The crude product was purified by silica gel column chromatography using hexanes/ethyl acetate (50/50) as the mobile phase yielding a diastereomeric mixture of **An-1NDI** (21 mg, 49 %). ¹H NMR (500 MHz, CD₂Cl₂): δ 8.81-8.87 (m, 4 H), 8.71-8.77 (m, 1H), 8.23-8.31 (m, 1 H), 8.14-8.22 (m, 1 H), 7.66-7.93 (m, 2 H), 7.50-7.65 (m, 2 H), 7.25-7.33 (m, 1 H), 4.20-4.27 (m, 2 H), 2.11-2.89 (m, 2 H), 1.73-1.87 (m, 2 H), -0.04-1.50 (m, 21 H). ¹³C NMR (125 MHz, CD₂Cl₂): δ 178.6, 178.3, 163.1, 163.0, 132.9, 132.8, 132.6, 132.0, 131.5, 131.4, 130.6, 130.6, 130.3, 129.5, 129.3, 129.0, 128.7, 128.0, 127.8, 127.7, 127.6, 127.3, 126.9, 125.8, 125.5, 115.3, 41.4, 40.8, 40.7, 32.3, 32.2, 29.7, 29.7, 28.4, 27.5, 24.5, 24.3, 23.1, 22.3, 22.1, 14.3. MALDI-TOF MS (*m/z*): calcd for C₄₄H₃₉N₃O₆Na⁺: 728.270; found: *m/z* 728.273 ([M+Na]⁺).



Br-An-1NDI: 10 mg of An-1NDI (0.014 mmol) was suspended in 10 ml of chloroform and 50 mL of acetic acid and the mixture was stirred. To this solution, 16 mg of bromine (0.10 mmol) was added dropwise. The reaction mixture was stirred for 12 h in the dark at 60°C. After completion of the reaction, the resulting material was extracted with dichloromethane and washed with the saturated solution of sodium bicarbonate, and combined organic layers were dried over anhydrous Na₂SO₄ and the filtrate was concentrated under reduced pressure. The crude product was purified by silica gel column chromatography using hexanes/ethyl acetate (50/50) as the mobile phase yielding a diastereomeric mixture of Br-An-1NDI (10 mg, 91%). ¹H NMR (500 MHz, CD₂Cl₂): δ 8.83-8.89 (m, 4 H), 8.75-8.82 (m, 1 H), 8.63-8.75 (m, 1 H), 7.55-8.00 (m, 4 H), 7.29-7.38 (m, 1 H), 4.20-4.29 (m, 2 H), 2.05-2.90 (m, 2 H), 1.72-1.85 (m, 2 H), -0.27-1.64 (m, 21 H). ¹³C NMR (125 MHz, CD₂Cl₂): 178.5, 178.1, 163.1, 163.1, 163.0, 162.9, 133.0, 132.5, 132.1, 131.8, 131.8, 131.5, 131.4, 130.3, 130.2, 130.0, 129.8, 129.6, 129.5, 129.2, 128.5, 128.3, 128.2, 128.1, 127.7, 127.7, 127.7, 127.5, 127.4, 127.3, 127.2, 127.1, 126.8, 126.7, 125.4, 125.0, 116.5, 115.9, 41.4, 40.7, 40.7, 32.2, 32.2, 30.1, 29.7, 29.7, 29.6, 28.5, 28.4, 27.5, 27.5, 24.6, 24.2, 23.1, 22.2, 22.1, 14.4, 14.3. MALDI-TOF MS (*m/z*): calcd for C₄₄H₃₇BrN₃O₆⁻: 782.187; found: *m/z* 782.162 ([M-H]⁻).



1NDI: 25 mg of Br-An-1NDI (0.025 mmol), 12.5 mg of 4-(dimethylamino)phenyl boronic acid (0.075 mmol), and 25 mg of potassium phosphate tribasic (0.12 mmol) were combined in 4 mL THF and this solution was purged with nitrogen for 15 min. After adding 3 mg of tetrakis(triphenylphosphine)palladium(0) (0.003 mmol) to the solution, the solution was purged with nitrogen for another 15 min. The solution was then heated at 70°C for 12 h. The solution was cooled and then the solvent was then removed by rotary evaporation. The crude product was purified by silica gel column chromatography using hexanes/ethyl acetate (50/50) as the mobile phase yielding 2.5 mg of a diastereomeric mixture of **1NDI** (12% yield). ¹H NMR (500 MHz, CDCl₃): δ 8.79-8.92 (m, 4 H), 7.87-7.99 (m, 3 H), 7,43-7.55 (m, 2H), 7.30-7.35 (m, 3H), 7.18-7.22 (m, 1H), 6.93-6.99 (m, 2H), 4.22-4.27 (m, 2 H), 3.09 (s, 6 H), 2.79-2.84 (m, 2 H), 1.75-1.81 (m, 3 H), -0.1-1.64 (m, 21 H). ¹³C NMR (125 MHz, CDCl₃): 178.3, 177.9, 162.6, 150.1, 140.6, 132.0, 131.9, 131.8, 131.7, 131.3, 129.9, 129.8, 128.6, 128.3, 128.2, 127.3, 127.0, 126.9, 126.8, 126.6, 125.7, 124.6, 124.3, 114.0, 112.2, 41.2, 40.0, 40.3, 31.8, 29.7, 29.3, 29.2, 28.1, 27.1, 24.2, 23.9, 22.7, 21.8, 21.1, 14.2, 14.1 MALDI-TOF MS (*m/z*): calcd forC₅₂H₄₈N₄O₆⁺: 824.357; found: *m/z* 824.346 ([M]⁺).



Scheme S2 Synthetic route to DMA-An

DMA-An: 27 mg of 9-bromo-10-methylanthracene (0.10 mmol), 50 mg of 4-(dimethylamino)phenylboronic acid (0.20 mmol), and 64 mg of cesium carbonate (0.20 mmol) were combined in 10 mL toluene and this solution was purged with argon for 15 min. After adding 5 mg of tetrakis(triphenylphosphine)palladium(0) (0.005 mmol) to the solution, the solution was purged with argon for another 15 min. The solution was then heated at 110°C for 24 h. The solution was cooled and then the solvent was then removed by rotary evaporation. The product was purified by silica gel column chromatography with DCM/hexanes (9/1) giving 7 mg of **DMA-An** (22% yield). (22% yield). ¹H NMR (500 MHz, CDCl₃): δ 8.32 (d, 2 H, *J* = 9.0 Hz), 7.79 (d, 2 H, *J* = 9.0 Hz), 7.44-7.51 (m, 2 H), 7.29-7.35 (m, 2 H), 7.26 (d, 2 H, *J* = 8.5 Hz), 6.92 (d, 2 H, *J* = 8.5 Hz), 3.15 (s, 3 H), 3.07 (s, 3 H). ¹³C NMR (125 MHz, CDCl₃): δ 149.7, 136.3, 132.1, 130.5, 129.8, 129.4, 128.1, 126.9, 124.9, 124.6, 124.4, 112.2, 40.7, 14.2. HRMS-ESI⁺ (m/z) calcd for C₂₃H₂₂N⁺ (M+H⁺): 312.1747, found: 312.1750.

3. Theory background

A simple Hamiltonian H for describing the donor D with energy E_D coupled to two acceptors A_1, A_2 with energy E_A and the coupling constant V is given in Equation S6-S7

$$H = E_{D}c_{D}^{\dagger}c_{D} + E_{A}c_{A_{1}}^{\dagger}c_{A_{1}} + E_{A}c_{A_{2}}^{\dagger}c_{A_{2}} + H_{V}$$
 Equation S6
$$H_{V} = Vc_{D}^{\dagger}c_{A} + Vc_{D}^{\dagger}c_{A} + H.c.$$

$$H_V = Vc_D^{\top}c_{A_1} + Vc_D^{\top}c_{A_2} + H.c.$$
 Equation S7

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 Equation S8-S9

$$H_V = \sqrt{2}Vc_D^{\dagger}c_{A_+} + H.c.$$
 Equation S8

$$c_{A_{+}} = (c_{A_{1}} + c_{A_{2}})/\sqrt{2}$$
 Equation S9

where only the superposition bonding state A_+ 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 A_+ and anti-bonding A_- states, but the donor still couples to only A_+ with normalized coupling $\sqrt{2}V$.

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 A_1 and A_2 are uncorrelated. This is equivalent to coupling the two acceptors to independent baths and represents the statistical or incoherent limit where the ET rate constant with two acceptors $k_{CS}(2)$ is twice that of the ET 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 A_+ 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^{5,6} to describe the dynamics of the system and the effect of quantum coherence on k_{CS} . In this model, the general donor-acceptor (DA) quantum system is

represented by a two-level system characterized by the energy difference ε_{DA} between the donor and acceptor and the coupling V_{DA} between the donor and the acceptor. The environment is a bosonic bath of harmonic oscillators each with mass m_i and frequency ω_i . The bath frequencies have a normal distribution around the bath characteristic frequency $\omega_c = 1/\tau_c$ where τ_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.⁵ The coupling between each mode of the bath and the system is V_{SB_i} which determines the spectral function and the reorganization energy of the bath. The spectral function of the bath J(E) is defined in Equations S10-11.

$$J(E) = \pi \sum_{i} \frac{g_{i}^{2}}{2m_{i}\omega_{i}} \delta(E - \hbar\omega_{i})$$
 Equation S10

$$g_i = V_{SB_i} \sqrt{(2m_i \omega_i)/\hbar}$$
 Equation S11

This function describes the frequency distribution of the bath and the strength of system-bath coupling. The reorganization energy of the bath λ_B is defined in Equation S12.

$$\lambda_B = \frac{1}{\pi} \int_0^\infty \frac{J(E)}{E} dE$$
 Equation S12

 λ_B measures the energy required for the bath harmonic modes to adjust to themselves when the charge is transferred to the acceptor.

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 Equations S13-14 where $E^2 = \varepsilon_{DA}^2 + V_{DA}^2$ and ε_{DA} is the instantaneous DA energy gap.⁶

$$k_{CS} \approx (V_{DA}^2 \kappa) / (\kappa^2 + \varepsilon_{DA}^2)$$
 Equation S13

$$\kappa(E) = \frac{f(E)}{2\hbar} \operatorname{coth}\left(\frac{E}{2k_BT}\right)$$
Equation S14

At low temperatures $\kappa \ll E$, V_{DA} and high driving force $\varepsilon_{DA} > V_{DA}$ 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 Equation S15.

$$k_{CS} \approx \left(V_{DA}^2 \kappa\right) / \varepsilon_{DA}^2$$
 Equation S15

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.

4. Additional steady-state optical spectroscopy

To characterize the electronic transitions associated with **DMA**⁺⁺, we performed a photolysis measurement on a control **DMA-An** compound (structure within inset of Figure S5). The sample was dissolved in 2-chlorobutane, brought to 90 K in a cryostat, and subsequently irradiated with ~ 45 mW (4.5 mJ/pulse) at 355 nm, using the third harmonic of a Quanta Ray Pro 350 laser (Spectra-Physics Inc.), for 30 minutes to promote electron transfer to the solvent. After accumulating substantial photolyzed product, an extinction spectrum was collected and is shown in Figure S5. In comparison to the steady-state absorption by the **DMA-An** compound, three new bands appear. We assign these transitions, located at 577, 628, and 689 nm, to absorption by **DMA**⁺⁺.



Figure S5. An extinction spectrum of photolyzed **DMA-An** (structure provided in inset). The three labeled electronic transitions correspond to absorption by **DMA**⁺⁺.

5. Computed geometries and energies

1NDI (neutral)

- E(0) = -2404.99010692378 hartree
- E(-1) = -2405.06225079 hartree

E(+1) = -2404.73501978 hartree

С	3.99468	0.18115	-0.02415	С	-3.27874	2.62313	-1.44834
С	3.24081	1.30449	0.36292	С	-4.61432	2.18811	-1.55246
С	3.3474	-1.00644	-0.41484	С	-5.16443	1.39341	-0.57129
С	1.91523	-1.06372	-0.42062	С	-2.84164	0.27506	2.76352
С	1.18182	0.05471	-0.04216	С	-4.16195	-0.19526	2.6352
С	1.81122	1.22901	0.35876	С	-4.92767	0.16504	1.54775
С	3.85498	2.53298	0.76922	С	-6.29693	-0.39452	1.39547
С	3.10443	3.6048	1.14923	N	-7.02478	0.02856	0.27948
С	1.68407	3.52696	1.16802	С	-6.55748	0.89522	-0.71237
С	1.06943	2.37825	0.78861	0	-7.26876	1.19714	-1.65011
С	4.07856	-2.16786	-0.82185	0	-6.75705	-1.19151	2.19039
С	3.43353	-3.30498	-1.20538	0	-0.55434	3.31252	-1.18572
С	2.01376	-3.36807	-1.20194	0	-0.21144	1.29575	2.89154
С	1.281	-2.28645	-0.82015	Ν	-0.14341	-2.35948	-0.84006
Ν	-0.36198	2.24846	0.82392	С	-0.89833	-2.34303	-2.02966
С	-1.0833	2.67651	-0.30082	С	-2.31244	-2.70543	-1.6282
С	-2.51557	2.27201	-0.35693	С	-2.37645	-2.33227	-0.15076
С	-3.06735	1.47399	0.67121	С	-0.94092	-2.47129	0.31476
С	-2.30234	1.09507	1.7974	0	-0.45511	-2.13001	-3.12956
С	-0.89134	1.5462	1.92263	0	-0.52097	-2.60006	1.43738
С	-4.39782	1.0192	0.55534	Н	0.09982	0.00364	-0.06467

Н	4.93766	2.59583	0.77045	Н	8.107	-0.39809	2.04706
Н	3.58601	4.52763	1.45568	Н	8.09339	1.14849	-1.98445
Н	1.0898	4.37567	1.48911	Н	5.66445	1.02617	-2.00224
Н	5.16221	-2.12504	-0.82359	Н	10.0979	0.97361	2.05896
Н	4.00058	-4.17666	-1.51552	Н	11.47491	0.33256	1.13919
Н	1.50713	-4.27779	-1.50718	Н	10.2237	-0.76758	1.71393
Н	-2.8264	3.22373	-2.22993	н	10.13156	2.14501	-1.11946
Н	-5.22184	2.45751	-2.4097	Н	10.19972	0.59778	-1.99582
Н	-2.22472	-0.01552	3.60647	Н	11.47991	1.01633	-0.8614
Н	-4.58788	-0.86081	3.3783	С	-3.48423	-3.10746	0.55829
С	-8.37176	-0.50229	0.0829	C	-4.69357	-3.25729	-0.40541
H	-8.61077	-1.13257	0.93596	C	-4.7437	-2.15366	-1.47792
н	-8,40595	-1.08445	-0.84079	C	-3.49885	-2.137	-2.40106
H	-9.08261	0.32137	0.00029	Ĥ	-2.34145	-3.80475	-1.68883
С	5,48431	0.24558	-0.00984	Н	-2.59127	-1.25335	-0.08272
Č	6.20952	-0.14616	1.11621	H	-3.77953	-2.58931	1.47341
Č	7 59545	-0.08548	1 14475	н	-3 11693	-4 09388	0.86167
Č	8 32485	0.36853	0.02839	н	-5 62455	-3 25088	0 17049
č	7 58879	0 77333	-1 10237	н	-4 64857	-4 23288	-0.9053
č	6 20233	0 70615	-1 11382	н	-4 81327	-1 1869	-0 97166
N	9 70991	0.40826	0.04264	Н	-5 6561	-2 25088	-2 07489
C	10 40046	0.40020	1 30253	н	-3 2856	-1 11152	-2 72361
č	10.40415	1 08138	-1 03370	н	-3 67030	-2 72/78	-3 30722
ц	5 67720	-0.50378	1 00351		-3.07038	-2.72470	-3.30722
11	5.07729	-0.50576	1.99001				
INI	DI (anion)						
E(-	1) = -2405.069	67126450 ha	rtree				
с`	4 00604	-0 20559	-0.04257	С	-0 82094	-3 26825	-1 25055
Ĉ	3 24116	0.20000	-0.07401	C	-2 28749	-3 13355	-0 88945
Ċ	3 37553	-1 46406	-0.03284	C	-2 27439	-2 12523	0.00040
č	1 04405	-1 53578	-0.00204	Ċ	_0.0401	-2 37775	0.20010
č	1 20206	-0.36153	-0.0023	Ő	-0.3401	-3 65738	-2 28264
č	1 81311	0.88540	-0.0304	Ő	-0.52337	-2 17368	2 04006
ĉ	3 83515	2 27845	-0.00713	Ц	0.12223	-0 30800	_0 1382
ĉ	3 05717	2.27040	-0.09349	Ц	1 01687	-0.39099	-0.1302
ĉ	1 6275	2 20615	-0.11344	и Ц	2 52204	2.30130	-0.09033
č	1.0370	2.30013	-0.09723		1 02070	4.37000	-0.13207
č	1.03302	2.0090	-0.07700		1.02079 5.10007	4.20375	-0.00301
C	4.11313	-2.09042	-0.01093		5.19907	-2.0440	0.00704
	3.47044	-3.09000	-0.01971		4.03443	-4.01003	-0.00696
	2.00034	-3.97041	-0.03651		1.00700	-4.93233	-0.0439
	1.3183	-2.82881	-0.0536	н	-2.8044	1.91994	-3.21175
	-0.39179	1.97359	-0.00194	н	-5.34699	1.00320	-3.04645
C	-1.11033	1.95833	-1.21/28	н	-2.35333	1.37239	3.49324
C	-2.55071	1.76889	-1.09612	H	-4.82947	1.00106	3.64951
C	-3.13937	1.58374	0.17668	C	-8.72672	0.67557	0.4938
C	-2.36802	1.581/2	1.36015	н	-8.98621	0.47659	1.53153
C	-0.93058	1.80728	1.29662	н	-8.97848	-0.17725	-0.14125
C	-4.55428	1.38589	0.26821	Н	-9.27395	1.54573	0.12108
С	-3.35372	1.77681	-2.25419	С	5.49483	-0.12229	-0.00459
С	-4.718	1.60615	-2.1627	С	6.18038	-0.06346	1.20896
С	-5.33084	1.40238	-0.9112	С	7.56532	0.02308	1.26046
С	-2.98209	1.37355	2.6096	С	8.33329	0.04701	0.08197
С	-4.34261	1.16956	2.69515	С	7.64013	-0.00148	-1.14105
С	-5.14098	1.17041	1.53486	С	6.25426	-0.08902	-1.17423
С	-6.57509	0.93271	1.64687	N	9.72624	0.10803	0.12518
Ν	-7.29488	0.92545	0.43955	С	10.35494	0.45705	1.38091
С	-6.76382	1.15693	-0.83724	С	10.43207	0.45471	-1.08981
0	-7.5119	1.13474	-1.81365	Н	5.61424	-0.07804	2.13621
0	-7.14974	0.73783	2.71669	Н	8.04345	0.07309	2.23147
0	-0.51405	2.09502	-2.27917	Н	8.17662	0.02805	-2.08194
0	-0.18979	1.85254	2.26935	Н	5.74693	-0.12388	-2.13444
Ν	-0.10175	-2.88297	-0.1075	Н	10.01832	1.42986	1.77488

н н н с с с с н 1ND Е(+1	11.43729 10.15296 10.11617 10.2811 11.50328 -3.56156 -4.75787 -4.43381 -3.28509 -2.57955 $\mathbf{I} (cation)$ $\mathbf{I} = -2404 \ 752$	0.49748 -0.30496 1.4247 -0.31065 0.50044 -2.16084 -2.35641 -1.92394 -2.73792 -4.10783	1.24114 2.14163 -1.50707 -1.85901 -0.8824 1.06958 0.09801 -1.34267 -1.9802 -0.46705		-2.17132 -3.66289 -3.52285 -5.62067 -5.06055 -4.15736 -5.33386 -2.78709 -3.66663	-1.12173 -1.23175 -2.97716 -1.78752 -3.41275 -0.8668 -1.9905 -2.13996 -3.63803	-0.18585 1.63496 1.80032 0.45934 0.09227 -1.33753 -1.96262 -2.75097 -2.47347
E(+1)2404.732	+38313308 Ila	luee				
00000	4.04444 3.29979 3.34405 1.91492 1.22032	-0.01105 1.21641 -1.26459 -1.27182 -0.06121	-0.05165 -0.1264 0.03554 0.06115 -0.00073	H H H H H H H	3.652 1.16394 5.08314 3.8366 1.35745	4.60888 4.50331 -2.55392 -4.63691 -4.6342	-0.15346 -0.21878 -0.11003 0.12443 0.23973
C	1.87391	1.16843	-0.1109	H	-2.66498	2.11397	-3.39302
C	3.91185	2.49251	-0.10363	H	-5.12573	1.58704	-3.3226
C	3.15624	3.64421	-0.16047	H	-2.38871	1.60678	3.29991
C	1.75158	3.59288	-0.19073	H	-4.85135	1.08366	3.35364
C	1.12441	2.37605	-0.1434	C	-8.61247	0.4772	0.06837
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C	3.30284	-3.69267	0.12187		-8.75222	-0.47814	-0.44197
C	1.90111	-3.69894	0.1795	H	-9.17777	1.24348	-0.46353
C	1.21208	-2.50872	0.11475	C	5.49229	0.01483	-0.04845
N	-0.30429	2.28358	-0.10306	C	6.24113	-0.67806	0.9339
C	-0.98161	2.28044	-1.34351	C	7.61228	-0.63608	0.96315
C	-2.4378	2.01098	-1.2809	C	8.34347	0.07395	-0.03068
C C C	-3.06246 -2.33736	1.78627 1.82243	-0.0308 1.18328	C C	7.59535 6.22326	0.75061 0.73715	-1.03574 -1.02281
C C	-0.66099 -4.44248 -3 16937	2.0077 1.49252 1.94818	0.0048	C	9.09491 10.44216 10.42413	-0.63472 0.8632	-0.02020 0.98864 -1 02825
C C	-4.54535	1.65083	-2.40868	н Н Н	5.71689	-1.20101	1.72767
C	-2.96908	1.57588	2.38393	H	8.10279	1.26894	-1.83918
C	-4.34537	1.28237	2.41524	H	5.6874	1.23843	-1.8229
C	-5.07044	1.24	1.24508	H	10.22499	-0.26264	1.9962
C	-6.52107	0.89278	1.29438	H	11.5083	-0.51118	0.8049
N	-7 19253	0.83314	0.07153	H	10.21075	-1 70453	0.94569
C	-6.61384	1.05576	-1.17842	H	10.12784	1.91736	-1.01832
O	-7.2679	0.94223	-2.19451	H	10.25849	0.45438	-2.03166
0	-7.0803	0.66079	2.34609	H	11.4902	0.81104	-0.81237
	-0.37183	2.46914	-2.37096	C	-3.55834	-3.66294	1.23836
	-0.18781	2.09689	2.16151	C	-4 75581	-3.4998	0.26633
N	-0.20428	-2.51817	0.0974	C	-4.81113	-2.09662	-0.36201
C	-0.9908	-2.08608	-0.99915	C	-3.5797	-1.79943	-1.25306
C	-2.386	-2.59578	-0.73256	H	-2.40494	-3.60794	-1.16481
C	-2.4234	-2.7432	0.78896	H	-2.5805	-1.7378	1.21249
	-0.99233	-3.0901	1.13359	H	-3.85081	-3.41038	2.26121
	-0.5722	-1.44839	-1.93241	H	-3.21968	-4.70412	1.25551
	-0.54284	-3.68602	2.07568	H	-5.6898	-3.70600	0.79597
н	0.14173	-0.07504	0.03892	H	-4.68567	-4.24605	-0.53456
Н	4.98706	2.57697		H	-4.86613	-1.35849	0.44784

Н	-3.34551	-0.73088	-1.24502				
2ND	I (neutral)						
E(0)	= -2875.0294	43093755 hart	tree				
E(-1) = -2875.10	164357 hartre	e				
E(+1) = -2874.779	969378 hartre	e				
С	4.8826	0.01172	0.00078	0	0.8846	-3.22665	0.94094
С	4.17887	1.0538	0.63923	С	-5.53551	-2.3269	1.1351
С	4.17808	-1.02905	-0.63919	N	-6.33172	-1.80859	0.10948
С	2.74783	-1.03375	-0.60517	С	-5.85824	-1.27908	-1.09119
С	2.06792	0.01337	-0.00046	0	-6.614	-0.84572	-1.94167
С	2.74859	1.06001	0.60431	0	-6.03922	-2.7308	2.16344
С	4.83461	2.11626	1.34173	Н	0.98528	0.01349	-0.00081
С	4.1219	3.11894	1.92948	Н	5.91709	2.10905	1.40576
С	2.70106	3.15223	1.84788	Н	4.63718	3.91303	2.46
С	2.04599	2.1532	1.20471	Н	2.14395	3.97149	2.2897
С	4.833	-2.0917	-1.34218	Н	5.91549	-2.08552	-1.40576
С	4.1196	-3.09326	-1.93101	Н	4.6343	-3.88745	-2.46199
С	2.69882	-3.12543	-1.84951	Н	2.14109	-3.9442	-2.29151
С	2.04445	-2.12617	-1.20587	Н	-1.1901	3.51626	-2.31512
Ν	0.61451	2.17164	1.0492	Н	-3.66362	3.32663	-2.7622
С	0.1368	2.70587	-0.16249	Н	-2.01114	0.33132	3.52559
С	-1.31757	2.5523	-0.42649	Н	-4.49569	0.2373	3.12456
С	-2.14675	1.92077	0.52696	Н	-2.01791	-0.32171	-3.53303
С	-1.6145	1.37701	1.71821	Н	-4.5053	-0.2537	-3.14377
С	-0.15439	1.4761	1.99654	Н	-1.19258	-3.50722	2.30671
С	-3.53482	1.842	0.28977	Н	-3.66994	-3.34222	2.74285
С	-1.85147	3.04364	-1.59724	С	-7.76153	1.75639	-0.39661
С	-3.23305	2.94075	-1.84452	С	-7.77124	-1.79983	0.36452
С	-4.0641	2.36399	-0.91007	Н	-8.25692	1.41272	0.5082
С	-2.44382	0.75592	2.62626	Н	-7.96891	1.07988	-1.22794
С	-3.83333	0.70148	2.40147	Н	-8.09335	2.76213	-0.65862
С	-4.3743	1.24988	1.2592	Н	-7.98273	-1.12517	1.19639
С	-5.84913	1.24531	1.0636	Н	-8.09938	-2.80725	0.62467
Ν	-6.32256	1.77219	-0.13836	Н	-8.2663	-1.45718	-0.54086
С	-5.52648	2.2953	-1.16167	С	6.37145	0.00905	0.00296
0	-6.02938	2.69264	-2.193	С	7.09189	-0.90907	0.76943
0	-6.60448	0.80245	1.90957	С	8.479	-0.92302	0.77429
0	0.88395	3.25545	-0.94074	С	9.21593	-0.00063	0.00515
0	0.35447	0.98595	2.98061	С	8.48662	0.91893	-0.77446
Ν	0.61299	-2.14578	-1.05026	С	7.09927	0.91871	-0.76657
С	-0.15738	-1.45279	-1.99821	N	10.59931	0.00482	0.01995
С	-1.61934	-1.36624	-1.72542	С	11.30211	-1.08395	0.66361
С	-2.15179	-1.91717	-0.53753	С	11.31342	0.83543	-0.92493
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С	0.13566	-2.68303	0.16023	Н	8.98684	-1.65853	1.38635
С	-2.4505	-0.75192	-2.63633	Н	9.00048	1.64016	-1.39849
С	-3.84162	-0.71223	-2.41827	Н	6.56564	1.63936	-1.38051
С	-4.38243	-1.26785	-1.27944	Н	11.08195	-1.11797	1.73744
С	-3.54166	-1.85302	-0.30689	Н	12.3771	-0.9306	0.55552
С	-1.85532	-3.04012	1.58646	Н	11.04942	-2.06446	0.23168
С	-3.23898	-2.9512	1.82753	Н	11.08895	1.89673	-0.76439
С	-4.07137	-2.38165	0.88987	Н	11.07638	0.58863	-1.97128
0	0.35149	-0.95657	-2.97926	Н	12.38667	0.70336	-0.77828

H -5.72863 -1.98325 -0.9479 H -3.77883 -2.06635 -2.29447

2NDI (anion)

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0	0.76308	-2.97112	1.65213	С	0.19554	2.88802	-0.5738
0	0.33347	-1.17262	-2.51464	С	1.96459	-2.16458	-0.6047
0	0.44563	1.59351	2.78395	С	2.58593	-3.29135	-1.03741
0	0.96985	3.37209	-1.38789	С	4.00536	-3.31651	-1.13579
0	-6.45055	0.72949	1.5422	С	4.75421	-2.23599	-0.77372
0	-5.90249	2.36606	-2.68118	С	2.08698	2.50786	0.86656
Ν	10.59899	-0.02389	-0.07833	С	2.77497	3.60103	1.28218
Ν	-6.4517	-2.01499	0.33229	С	4.19594	3.55339	1.35824
Ν	0.53439	-2.12287	-0.45308	С	4.88897	2.43879	0.98855
Ν	-6.15506	1.60681	-0.55265	С	2.77393	1.30236	0.5048
Ν	0.664	2.51402	0.70741	С	2.06194	0.17031	0.13605
С	11.25729	0.51609	-1.24848	С	2.70801	-0.99574	-0.24385
С	11.29395	-1.05389	0.66219	С	4.13801	-1.03483	-0.29394
С	7.07361	0.81647	-0.87185	С	4.20372	1.26805	0.52717
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С	9.20596	-0.00355	-0.03675	Н	12.33643	0.3839	-1.14524
С	8.48886	-0.76161	0.90662	Н	10.93516	0.03097	-2.18405
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2NDI (cation)

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С	-1.62068	1.57892	1.40734	Н	1.01844	-0.07179	-0.03981

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