Supporting Information for:

Role of Bridge Energetics on the Preference for Hole or Electron Transfer Leading to Charge Recombination in Donor-Bridge-Acceptor Molecules

Department of Chemistry and Argonne-Northwestern Solar Energy Research (ANSER) Center

Northwestern University, Evanston, Illinois 60208-3113

Michael T. Colvin, Annie Butler Ricks, and Michael R. Wasielewski*

Email: m-wasielewski@northwestern.edu

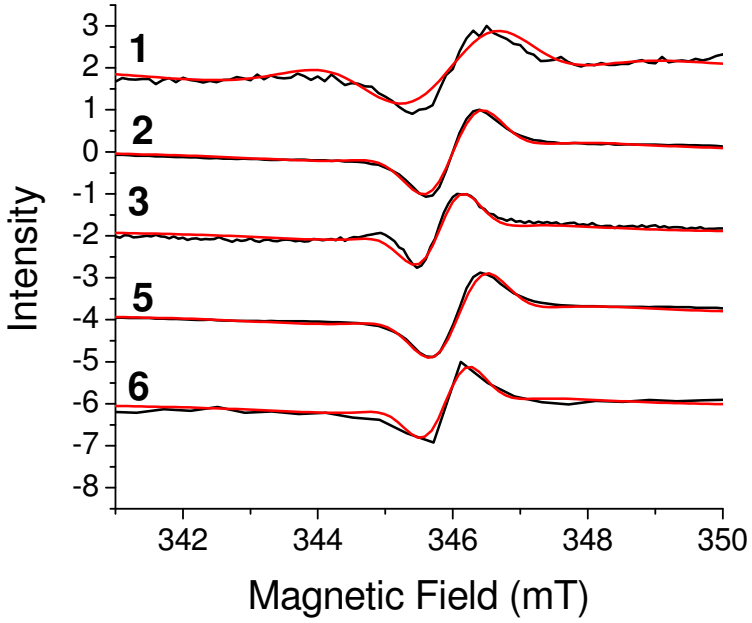

Figure S1. Time-resolved EPR of **1-3, 5** and **6** in toluene at 85 K, 150 ns after 7 ns 416 nm pulse.

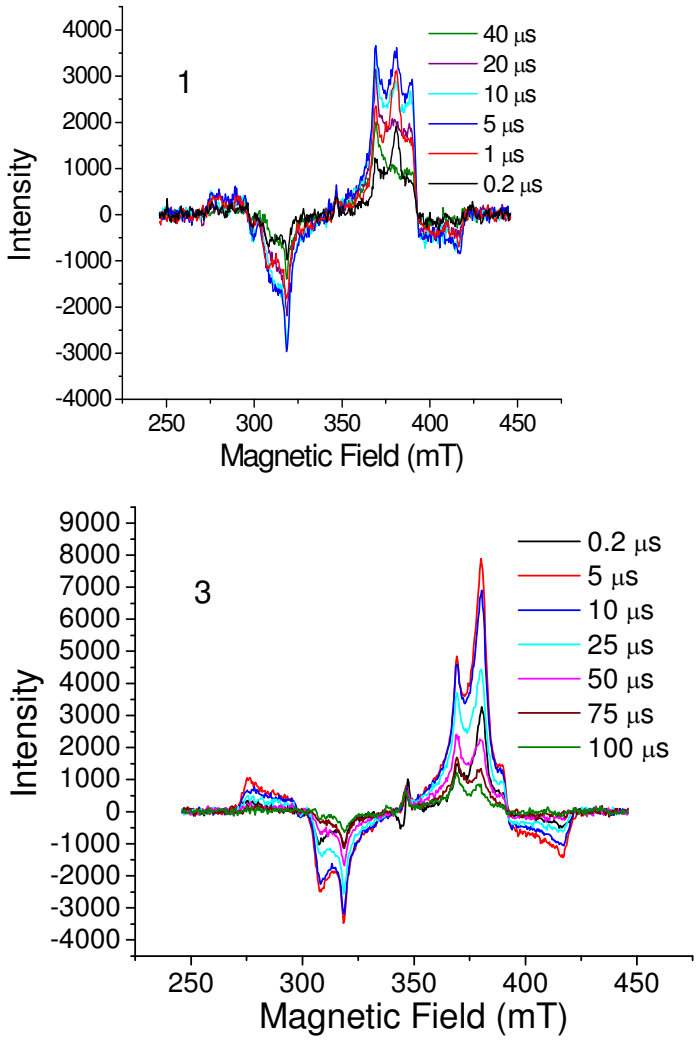

Figure S2. TREPR spectra of **1** and **3** in toluene at 85 K at times indicated.

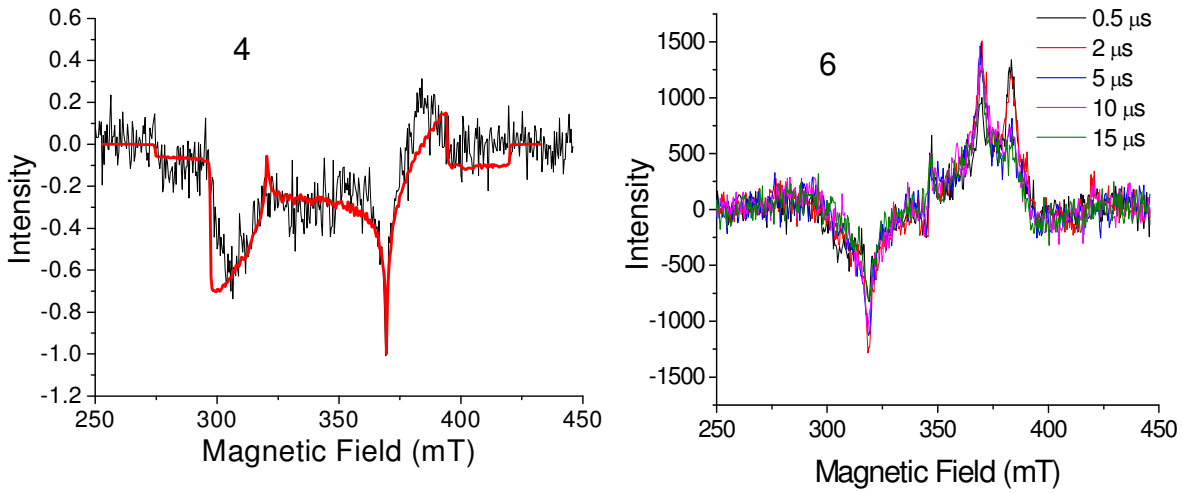

Figure S3. TREPR spectra in toluene at 85 K of **4** at 0.5 μs and **6** at the times indicated.

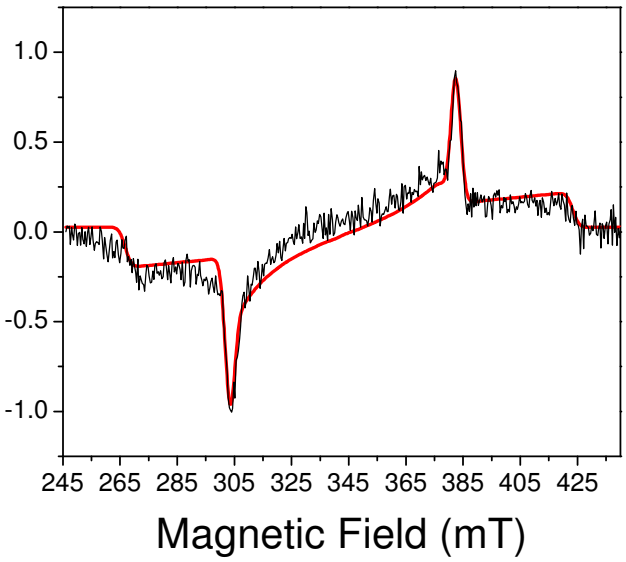

Figure S4. TREPR of FN_2[1] obtained 200 ns after a 10-Hz repetition 7 ns, 1.0mJ/pulse, 416-nm laser flash at 85 K, simulation shown in red.

Table S1. TREPR simulation parameters for **4**.

Compound	D (mT)	E (mT)	Ax	Ay	Az	T_{+1}-T_0	SO/RP
4	77.0	-8.5	0.3	0.1	0.19	1:0.45	0.73

Table S2. Simulation parameters for the triplet shown in Figure S4.

Compound	D	E	A_x	A_y	A_z
FN_2	78 mT	-6 mT	0.8	0.33	0.38

Radical Ion Pair Energies

Given that photoexcitation of DMJ-An results in quantitative charge separation to produce $DMJ^{+\bullet}$-$An^{-\bullet}$ with a spectroscopically determined energy of 2.89 eV in toluene,[2] the energy levels for the charge separated states, $DMJ^{+\bullet}$-An-PE_nP-$NI^{-\bullet}$, DMJ-An-$PE_nP^{+\bullet}$-$NI^{-\bullet}$, DMJ-$An^{+\bullet}$-PE_nP-$NI^{-\bullet}$, and $DMJ^{+\bullet}$-An-$PE_nP^{-\bullet}$NI and $DMJ^{+\bullet}$-An-FN_n-$NI^{-\bullet}$, DMJ-An-$FN_n^{+\bullet}$-$NI^{-\bullet}$, DMJ-$An^{+\bullet}$-FN_n-$NI^{-\bullet}$, and $DMJ^{+\bullet}$-An-$FN_n^{-\bullet}$NI were determined in toluene using equation S1.

$$\Delta G_F = \Delta G_I + sign\,(E_I - E_F) + \frac{e^2}{\varepsilon_s}\left(\frac{1}{r_1} - \frac{1}{r_F}\right) \qquad \text{(S1)}$$

where ΔG_I and ΔG_F are the energies above ground state for the initial and final ion pairs, respectively, E_I and E_F are the redox potentials for the initial and final ions, respectively, between which the electron is transferred, r_I and r_F are the initial and final ion pair distances, respectively, e is the electronic charge, and ε_S is the static dielectric constant of the solvent (ε_S = 2.38 for toluene) and the sign = (-) if $E_F > E_I$ and the sign = (+) if $E_I > E_F$. The $DMJ^{+\bullet}$-$An^{-\bullet}$ distance is 5.6 Å.[3] The distances r_I and r_F between the donor, bridge, and acceptor components were determined from the energy minimized structures of **1-6** determined with density functional theory (DFT) using Becke's[4] three parameter hybrid functional with Lee, Yang, and Parr[5]

correction functional (B3LYP) and the STO-3G basis set. The one-electron oxidation potential for DMJ is 0.63 vs. SCE,[6] while the one-electron reduction potentials for An and NI are -1.97 V[7] vs. SCE and -0.53 V[8] vs. SCE, respectively. The one-electron oxidation potentials for An, FN, FN_2, FN_3, PE_1P, PE_2P, PE_2P are 1.16, 2.11, 2.00, 1.57, 2.08, 2.00, and 1.90 V vs. SCE, respectively.[9] The one-electron reduction potentials of FN and FN_2 alone as well as FN_3 within DMJ-An-FN_n-NI (FN_3 itself is not soluble) were measured at a platinum electrode in DMF/0.1 tetra-n-butylammonium hexafluorophosphate to yield $E_{1/2}$ = -1.27, -1.14, and -1.08 V vs. SCE, respectively, using apparatus described previously.[6] The $E_{1/2}$ values for FN and FN_2 agree very well with those reported in acetonitrile.[10] The one-electron reduction potential for PE_1P is -2.26 V vs. SCE,[11] and that of PE_3P is approximately -2.3 V vs. SCE,[12] so that the reduction potential of PE_2P is also assumed to be about -2.3 V vs. SCE. The results of these ion pair energy calculations are given in Table S3 and illustrated in Figure 5 of the main text.

Table S3. Distances and energies of all intermediate states of **1-6**, calculated from Eq. S1.

	r_{An-NI}	r_{DMJ-NI}	r_{DMJ-B}	r_{B-NI}	$-\Delta G_{DMJ^+NI^-}$	$-\Delta G_{DMJ^+B^-}$	$-\Delta G_{B^+NI^-}$	$-\Delta G_{An^+NI^-}$
1	17.9	23.7	13.7	10.1	2.29	3.86	3.39	2.73
2	24.9	30.7	17.2	13.5	2.34	3.95	3.46	2.83
3	31.9	37.7	20.7	17.0	2.38	4.01	3.49	2.88
4	10.7	20.7	12.4	8.7	2.25	2.78	3.32	2.67
5	23.5	29.3	20.0	12.8	2.33	2.84	3.44	2.81
6	31.9	37.6	28.1	17.1	2.80	2.87	3.13	2.88

References:

(1)Scott, A. M.; Ricks, A. B.; Colvin, M. T.; Wasielewski, M. R. *Angew. Chem., Int. Ed.* **2010**, *49*, 2904-2908.
(2)Dance, Z. E. X.; Ahrens, M. J.; Vega, A. M.; Ricks, A. B.; McCamant, D. W.; Ratner, M. A.; Wasielewski, M. R. *J. Am. Chem. Soc.* **2008**, *130*, 830-832.
(3)Lockard, J. V.; Butler Ricks, A.; Co, D. T.; Wasielewski, M. R. *J. Phys. Chem. Lett.* **2010**, *1*, 215-218.
(4)Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 1372-1377.
(5)Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785-789.
(6)Dance, Z. E. X.; Ahrens, M. J.; Vega, A. M.; Ricks, A. B.; McCamant, D. W.; Ratner, M. A.; Wasielewski, M. R. *J. Am. Chem. Soc.* **2008**, *130*, 830-832.
(7)Parker, V. D. *J. Am. Chem. Soc.* **1976**, *98*, 98-103.
(8)Gosztola, D.; Niemczyk, M. P.; Svec, W.; Lukas, A. S.; Wasielewski, M. R. *J. Phys. Chem. A* **2000**, *104*, 6545–6551.
(9)(a)Banerjee, M.; Shukla, R.; Rathore, R. *J. Am. Chem. Soc.* **2009**, *131*, 1780-1786;
(b)Meerholz, K.; Heinze, J. *Electrochim. Acta* **1996**, *41*, 1839-1854.
(10)Uckert, F.; Setayesh, S.; Mullen, K. *Macromolecules* **1999**, *32*, 4519-4524.
(11)Amatore, C.; Galli, C.; Gentili, P.; Guarnieri, A.; Schottland, E.; Rappoport, Z. *J. Chem. Soc., Perkin Trans. 2* **1995**, 2341-2350.
(12)Matsuo, D.; Yang, X.; Hamada, A.; Morimoto, K.; Kato, T.; Yahiro, M.; Adachi, C.; Orita, A.; Otera, J. *Chem. Lett.* **2010**, *39*, 1300-1302.