Electronic Supplementary Material (ESI) for Faraday Discussions.

Supporting Information

Quantum Interferences Among Dexter Energy Transfer Pathways

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S1. Cartesian coordinates of the calculated molecular assemblies

Table S1. The Cartesian coordinates of the molecular assemblies calculated in the main text. (xyz coordinates in Angstroms)

Stacking-Nap-Nap (3.5 Å)

C	0.000000	0.718176	0.0000
C	0.000000	-0.718176	0.0000
C	-1.247217	1.404589	0.0000
C	-1.247217	-1.404589	0.0000
C	-2.438207	-0.709314	0.0000
H	-3.388297	-1.249729	0.0000
C	-2.438207	0.709314	0.0000
H	-3.388297	1.249729	0.0000
H	-1.245484	2.498243	0.0000
H	-1.245484	-2.498243	0.0000
C	1.247217	1.404589	0.0000
C	1.247217	-1.404589	0.0000
C	2.438207	-0.709314	0.0000
H	3.388297	-1.249729	0.0000
C	2.438207	0.709314	0.0000
H	3.388297	1.249729	0.0000
H	1.245484	2.498243	0.0000
H	1.245484	-2.498243	0.0000
C	0.000000	0.718176	-3.500000
C	0.000000	-0.718176	-3.500000
C	-1.247217	1.404589	-3.500000
C	-1.247217	-1.404589	-3.500000
C	-2.438207	-0.709314	-3.500000
H	-3.388297	-1.249729	-3.500000
C	-2.438207	0.709314	-3.500000
H	-3.388297	1.249729	-3.500000
H	-1.245484	2.498243	-3.500000
H	-1.245484	-2.498243	-3.500000
C	1.247217	1.404589	-3.500000
C	1.247217	-1.404589	-3.500000
C	2.438207	-0.709314	-3.500000
H	3.388297	-1.249729	-3.500000
C	2.438207	0.709314	-3.500000
H	3.388297	1.249729	-3.500000
H	1.245484	2.498243	-3.500000
H	1.245484	-2.498243	-3.500000

Stacking-Nap-Nap (7.0 Å)

C	0.000000	0.718176	0.0000
C	0.000000	-0.718176	0.0000
C	-1.247217	1.404589	0.0000
C	-1.247217	-1.404589	0.0000
C	-2.438207	-0.709314	0.0000
H	-3.388297	-1.249729	0.0000
C	-2.438207	0.709314	0.0000
H	-3.388297	1.249729	0.0000
H	-1.245484	2.498243	0.0000
H	-1.245484	-2.498243	0.0000
C	1.247217	1.404589	0.0000
C	1.247217	-1.404589	0.0000
C	2.438207	-0.709314	0.0000
H	3.388297	-1.249729	0.0000
C	2.438207	0.709314	0.0000
H	3.388297	1.249729	0.0000
H	1.245484	2.498243	0.0000
H	1.245484	-2.498243	0.0000
C	0.000000	0.718176	-7.000000
C	0.000000	-0.718176	-7.000000
C	-1.247217	1.404589	-7.000000
C	-1.247217	-1.404589	-7.000000
C	-2.438207	-0.709314	-7.000000
H	-3.388297	-1.249729	-7.000000
C	-2.438207	0.709314	-7.000000
H	-3.388297	1.249729	-7.000000
H	-1.245484	2.498243	-7.000000
H	-1.245484	-2.498243	-7.000000
C	1.247217	1.404589	-7.000000
C	1.247217	-1.404589	-7.000000
C	2.438207	-0.709314	-7.000000
H	3.388297	-1.249729	-7.000000
C	2.438207	0.709314	-7.000000
H	3.388297	1.249729	-7.000000
H	1.245484	2.498243	-7.000000
H	1.245484	-2.498243	-7.000000

Zigzag-Nap-Nap (7.0 Å)

C	7.361000	0.718176	3.500000
C	7.361000	-0.718176	3.500000
C	6.113783	1.404589	3.500000
C	6.113783	-1.404589	3.500000
C	4.922793	-0.709314	3.500000
H	3.972703	-1.249729	3.500000
C	4.922793	0.709314	3.500000
H	3.972703	1.249729	3.500000
H	6.115516	2.498243	3.500000
H	6.115516	-2.498243	3.500000
C	8.608217	1.404589	3.500000
C	8.608217	-1.404589	3.500000
C	9.799207	-0.709314	3.500000
H	10.749297	-1.249729	3.500000
C	9.799207	0.709314	3.500000
H	10.749297	1.249729	3.500000
H	8.606484	2.498243	3.500000
H	8.606484	-2.498243	3.500000
C	0.000000	0.718176	-3.500000
C	0.000000	-0.718176	-3.500000
C	-1.247217	1.404589	-3.500000
C	-1.247217	-1.404589	-3.500000
C	-2.438207	-0.709314	-3.500000
H	-3.388297	-1.249729	-3.500000
C	-2.438207	0.709314	-3.500000
H	-3.388297	1.249729	-3.500000
H	-1.245484	2.498243	-3.500000
H	-1.245484	-2.498243	-3.500000
C	1.247217	1.404589	-3.500000
C	1.247217	-1.404589	-3.500000
C	2.438207	-0.709314	-3.500000
H	3.388297	-1.249729	-3.500000
C	2.438207	0.709314	-3.500000
H	3.388297	1.249729	-3.500000
H	1.245484	2.498243	-3.500000
H	1.245484	-2.498243	-3.500000

Sandwich-Nap-Et-Nap

C	0.000000	0.718176	3.500000
C	0.000000	-0.718176	3.500000
C	-1.247217	1.404589	3.500000
C	-1.247217	-1.404589	3.500000
C	-2.438207	-0.709314	3.500000
H	-3.388297	-1.249729	3.500000
C	-2.438207	0.709314	3.500000
H	-3.388297	1.249729	3.500000
H	-1.245484	2.498243	3.500000
H	-1.245484	-2.498243	3.500000
C	1.247217	1.404589	3.500000
C	1.247217	-1.404589	3.500000
C	2.438207	-0.709314	3.500000
H	3.388297	-1.249729	3.500000
C	2.438207	0.709314	3.500000
H	3.388297	1.249729	3.500000
H	1.245484	2.498243	3.500000
H	1.245484	-2.498243	3.500000
C	4.578439	-1.916160	0.0
H	4.623460	-3.009774	0.0
H	5.536987	-1.387387	0.0
C	3.417040	-1.262470	0.0
H	3.372025	-0.168845	0.0
H	2.458492	-1.791242	0.0
C	0.000000	0.718176	-3.500000
C	0.000000	-0.718176	-3.500000
C	-1.247217	1.404589	-3.500000
C	-1.247217	-1.404589	-3.500000
C	-2.438207	-0.709314	-3.500000
H	-3.388297	-1.249729	-3.500000
C	-2.438207	0.709314	-3.500000
H	-3.388297	1.249729	-3.500000
H	-1.245484	2.498243	-3.500000
H	-1.245484	-2.498243	-3.500000
C	1.247217	1.404589	-3.500000
C	1.247217	-1.404589	-3.500000
C	2.438207	-0.709314	-3.500000
H	3.388297	-1.249729	-3.500000
C	2.438207	0.709314	-3.500000
H	3.388297	1.249729	-3.500000
H	1.245484	2.498243	-3.500000
H	1.245484	-2.498243	-3.500000

Zigzag-Nap-Et-Nap

C	7.361000	0.718176	3.500000
C	7.361000	-0.718176	3.500000
C	6.113783	1.404589	3.500000
C	6.113783	-1.404589	3.500000
C	4.922793	-0.709314	3.500000
H	3.972703	-1.249729	3.500000
C	4.922793	0.709314	3.500000
H	3.972703	1.249729	3.500000
H	6.115516	2.498243	3.500000
H	6.115516	-2.498243	3.500000
C	8.608217	1.404589	3.500000
C	8.608217	-1.404589	3.500000
C	9.799207	-0.709314	3.500000
H	10.749297	-1.249729	3.500000
C	9.799207	0.709314	3.500000
H	10.749297	1.249729	3.500000
H	8.606484	2.498243	3.500000
H	8.606484	-2.498243	3.500000
C	4.346997	2.150000	0.000000
H	4.922923	3.080982	0.000000
H	4.922909	1.219006	0.000000
C	3.014003	2.150000	0.000000
H	2.438077	1.219006	0.000000
H	2.438091	3.080994	0.000000
C	0.000000	0.718176	-3.500000
C	0.000000	-0.718176	-3.500000
C	-1.247217	1.404589	-3.500000
C	-1.247217	-1.404589	-3.500000
C	-2.438207	-0.709314	-3.500000
H	-3.388297	-1.249729	-3.500000
C	-2.438207	0.709314	-3.500000
H	-3.388297	1.249729	-3.500000
H	-1.245484	2.498243	-3.500000
H	-1.245484	-2.498243	-3.500000
C	1.247217	1.404589	-3.500000
C	1.247217	-1.404589	-3.500000
C	2.438207	-0.709314	-3.500000
H	3.388297	-1.249729	-3.500000
C	2.438207	0.709314	-3.500000
H	3.388297	1.249729	-3.500000
H	1.245484	2.498243	-3.500000
H	1.245484	-2.498243	-3.500000

Sandwich-Nap-Et□/Et□-Nap

C	0.000000	0.718176	3.500000
C	0.000000	-0.718176	3.500000
C	-1.247217	1.404589	3.500000
C	-1.247217	-1.404589	3.500000
C	-2.438207	-0.709314	3.500000
H	-3.388297	-1.249729	3.500000
C	-2.438207	0.709314	3.500000
H	-3.388297	1.249729	3.500000
H	-1.245484	2.498243	3.500000
H	-1.245484	-2.498243	3.500000
C	1.247217	1.404589	3.500000
C	1.247217	-1.404589	3.500000
C	2.438207	-0.709314	3.500000
H	3.388297	-1.249729	3.500000
C	2.438207	0.709314	3.500000
H	3.388297	1.249729	3.500000
H	1.245484	2.498243	3.500000
H	1.245484	-2.498243	3.500000
C	4.57843897	-1.91615958	0.0
H	4.62345964	-3.00977385	0.0
H	5.53698722	-1.38738744	0.0
C	3.41703994	-1.26246950	0.0
H	3.37202514	-0.16884480	0.0
H	2.45849169	-1.79124165	0.0
C	-4.57843897	1.91615958	0.0
H	-4.62345964	3.00977385	0.0
H	-5.53698722	1.38738744	0.0
C	-3.41703994	1.26246950	0.0
H	-3.37202514	0.16884480	0.0
H	-2.45849169	1.79124165	0.0
C	0.000000	0.718176	-3.500000
C	0.000000	-0.718176	-3.500000
C	-1.247217	1.404589	-3.500000
C	-1.247217	-1.404589	-3.500000
C	-2.438207	-0.709314	-3.500000
H	-3.388297	-1.249729	-3.500000
C	-2.438207	0.709314	-3.500000
H	-3.388297	1.249729	-3.500000
H	-1.245484	2.498243	-3.500000
H	-1.245484	-2.498243	-3.500000
C	1.247217	1.404589	-3.500000
C	1.247217	-1.404589	-3.500000
C	2.438207	-0.709314	-3.500000
H	3.388297	-1.249729	-3.500000
C	2.438207	0.709314	-3.500000
H	3.388297	1.249729	-3.500000
H	1.245484	2.498243	-3.500000
H	1.245484	-2.498243	-3.500000

S2. Diabatic Hamiltonian matrix with state energies and couplings from the CDFT-CI calculation

Table S2. Sandwich-Nap-Nap-3.0 Å structure

Energy /eV	^{3}Na-^{1}Na	Na^{-1}-Na^{+1}	Na^{+1}-Na^{-1}	^{1}Na-^{3}Na
^{3}Na-^{1}Na	0.0	0.668	0.603	-0.136
Na^{-1}-Na^{+1}	0.668	2.31	-0.359	0.603
Na^{+1}-Na^{-1}	0.603	-0.359	2.31	0.668
1Na-^{3}Na	-0.136	0.603	0.668	0.0

Table S3. Sandwich-Nap-Nap-7.0 Å structure

Energy /eV	^{3}Na-^{1}Na	Na^{-1}-Na^{+1}	Na^{+1}-Na^{-1}	^{1}Na-^{3}Na
^{3}Na-^{1}Na	0.0	0.00245	0.00465	-1.09E-5
Na^{-1}-Na^{+1}	0.00245	3.30	-1.90E-5	0.00465
Na^{+1}-Na^{-1}	0.00465	-1.90E-5	3.30	0.00245
1Na-^{3}Na	-1.09E-5	0.00465	0.00245	0.0

Table S4. Zigzag-Nap-Nap structure

Energy /eV	^{3}Na-^{1}Na	Na^{-1}-Na^{+1}	Na^{+1}-Na^{-1}	^{1}Na-^{3}Na
^{3}Na-^{1}Na	0.0	3.54E-4	0.00181	-5.58E-8
Na^{-1}-Na^{+1}	3.54E-4	3.72	-2.72E-6	0.00181
Na^{+1}-Na^{-1}	0.00181	-2.72E-6	3.72	3.54E-4
1Na-^{3}Na	-5.58E-8	0.00181	3.54E-4	0.0

Table S5. Sandwich-Nap-Et-Nap structure

Energy /eV	^{3}Na-^{1}Et-^{1}Na (1)	Na^{-1}-Et^{+1}-^{1}Na (2)	Na^{+1}-Et^{-1}-^{1}Na (3)	Na^{-1}-^{1}Et-Na^{+1} (4)	^{1}Na-^{3}Et-^{1}Na (5)	Na^{+1}-^{1}Et-Na^{-1} (6)	^{1}Na-Et^{-1}-Na^{+1} (7)	^{1}Na-Et^{+1}-Na^{-1} (8)	^{1}Na-^{1}Et-^{3}Na (9)
^{3}Na-^{1}Et-^{1}Na (1)	0	0.0955	0.0608	-0.00448	0.00264	0.00337	4.90E-4	-6.53E-4	1.09E-5
Na^{-1}-Et^{+1}-^{1}Na (2)	0.0955	5.44	-0.00701	0.108	-0.0960	-0.00110	-0.00841	0.00762	-6.53E-4
Na^{+1}-Et^{-1}-^{1}Na (3)	0.0608	-0.00701	4.68	3.26E-4	-0.0828	0.0923	3.62E-4	-0.00841	4.90E-4

Na^{-1}-^{1}Et-Na^{+1} (4)	-0.00448	0.108	3.26E-4	3.32	0.00365	6.53E-5	0.0923	-0.00110	0.00337
^{1}Na-^{3}Et-^{1}Na (5)	0.00264	-0.0960	-0.0828	0.00365	1.68	0.00365	-0.0828	-0.0960	0.00264
Na^{+1}-^{1}Et-Na^{-1} (6)	0.00337	-0.00110	0.0923	6.53E-5	0.00365	3.22	3.26E-4	0.107	-0.00448
^{1}Na-Et^{-1}-Na^{+1} (7)	4.90E-4	-0.00841	3.62E-4	0.0923	-0.0828	3.26E-4	4.68	-0.00701	0.0608
^{1}Na-Et^{+1}-Na^{-1} (8)	-6.53E-4	0.00762	-0.00841	-0.00110	-0.0960	0.107	-0.00701	5.44	0.0955
^{1}Na-^{1}Et-^{3}Na (9)	1.09E-5	-6.53E-4	4.90E-4	0.00337	0.00264	-0.00448	0.0608	0.0955	0

Table S6. Zigzag-Nap-Et-Nap structure

Energy /eV	^{3}Na-^{1}Et-^{1}Na (1)	Na^{-1}-Et^{+1}-^{1}Na (2)	Na^{+1}-Et^{-1}-^{1}Na (3)	Na^{-1}-^{1}Et-Na^{+1} (4)	^{1}Na-^{3}Et-^{1}Na (5)	Na^{+1}-^{1}Et-Na^{-1} (6)	^{1}Na-Et^{-1}-Na^{+1} (7)	^{1}Na-Et^{+1}-Na^{-1} (8)	^{1}Na-^{1}Et-^{3}Na (9)
Na-^{1}Et-^{1}Na (1)	0	0.118	0.0415	-0.00663	-0.00201	7.13E-4	-3.35E-4	-1.31E-4	5.44E-6
Na^{-1}-Et^{+1}-^{1}Na (2)	0.118	5.39	-0.00414	0.128	0.0556	-1.60E-4	0.00501	0.00112	-1.31E-4
Na^{+1}-Et^{-1}-^{1}Na (3)	0.0415	-0.00414	4.89	2.61E-4	0.0964	-0.0701	0.0071	0.00501	-3.35E-4
Na^{-1}-^{1}Et-Na^{+1} (4)	-0.00663	0.128	2.61E-4	3.71	-0.00320	5.44E-6	-0.0701	-1.60E-4	7.13E-4
^{1}Na-^{3}Et-^{1}Na (5)	-0.00201	0.0556	0.0964	-0.00320	1.71	0.00320	-0.0964	-0.0556	0.00201
Na^{+1}-^{1}Et-Na^{-1} (6)	7.13E-4	-1.6E-4	-0.0701	5.44E-6	0.00320	3.71	2.61E-4	0.128	-0.00663
^{1}Na-Et^{-1}-Na^{+1} (7)	-3.35E-4	0.00501	0.0071	-0.0701	-0.0964	2.61E-4	4.89	-0.00414	0.0415
^{1}Na-Et^{+1}-Na^{-1} (8)	-1.31E-4	0.00112	0.00501	-1.6E-4	-0.0556	0.128	-0.00414	5.39	0.118
^{1}Na-^{1}Et-^{3}Na (9)	5.44E-6	-1.31E-4	-3.35E-4	7.13E-4	0.00201	-0.00663	0.0415	0.118	0

Table S7. Sandwich-Nap-EtU-EtL-Nap structure

The state numbering corresponds to: (1) Initial ^{3}Na-^{1}Et-^{1}Et-^{1}Na; (2) Na^{-1}-Et^{+1}-^{1}Et -^{1}Na; (3) Na^{+1}-Et^{-1}-^{1}Et -^{1}Na; (4) Na^{-1}-^{1}Et-^{1}Et -Na^{+1}; (5) ^{1}Na-^{3}Et-^{1}Et -^{1}Na; (6) Na^{+1}-^{1}Et-^{1}Et -Na^{-1}; (7) ^{1}Na-Et^{-1}-^{1}Et -Na^{+1}; (8) ^{1}Na-Et^{+1}-^{1}Et -Na^{-1}; (9) ^{1}Na-Et^{-1} -Et^{+1}-^{1}Na; (10) ^{1}Na-Et^{+1} -Et^{-1}-^{1}Na; (9) Na^{-1}-^{1}Et -Et^{+1}-^{1}Na; (12) Na^{+1}-^{1}Et -Et^{-1}-^{1}Na; (13) ^{1}Na-^{1}Et -^{3}Et-^{1}Na; (14) ^{1}Na-^{1}Et -Et^{-1}-Na^{+1}; (15) ^{1}Na-^{1}Et -Et^{+1}-Na^{-1}; (16) Final ^{1}Na-^{1}Et-^{1}Et ^{3}Na.

Energy /eV	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**	**15**	**16**
1	0.00	-0.0940	0.0603	-0.00704	0.00261	-0.00229	6.18E-4	-2.45E-4	-0.00622	-0.00253	-0.0940	-0.0603	-0.00261	-6.18E-4	-2.45E-4	8.16E-6
2	-0.094	5.46	0.00686	-0.110	0.0910	-3.32E-4	0.00766	-0.00341	-7.92E-4	-0.0450	-0.0145	-0.00409	-3.59E-4	-0.00587	-3.26E-5	2.45E-4

3	0.0603	0.00686	4.66	4.19E-4	-0.0846	-0.0830	1.44E-4	-0.00766	-0.00753	-0.00148	0.00409	-0.0184	2.80E-4	2.85E-4	-0.00587	6.18E-4
4	-0.00704	-0.11	4.19E-4	3.36	0.00362	-2.45E-5	-0.0830	-3.32E-4	-0.00648	-0.00313	-0.110	-4.19E-4	-0.00362	-0.0830	-3.32E-4	0.00229
5	0.00261	0.091	-0.0846	0.00362	1.67	-0.00362	-0.0846	-0.0910	0.00827	0.00783	3.59E-4	2.80E-4	1.63E-5	2.80E-4	-3.59E-4	0.00261
6	-0.00229	-3.32E-4	-0.083	-2.45E-5	-0.00362	3.36	-4.19E-4	-0.110	0.00313	0.00648	-3.32E-4	0.0830	0.00362	4.19E-4	-0.110	0.00704
7	6.18E-4	0.00766	1.44E-4	-0.083	-0.0846	-4.19E-4	4.66	-0.00686	0.107	0.00236	0.00587	2.86E-4	2.80E-4	-0.0184	-0.00409	0.0603
8	-2.45E-4	-0.00341	-0.00766	-3.32E-4	-0.091	-0.11	-0.00686	5.46	4.68E-4	0.0963	-3.26E-5	0.00587	3.59E-4	0.00409	-0.0145	0.0940
9	-0.00622	-7.92E-4	-0.00753	-0.00648	0.00827	0.00313	0.107	4.68E-4	7.94	-1.77E-4	-0.0963	-0.00236	-0.00783	0.00148	0.0450	-0.00253
10	-0.00253	-0.045	-0.00148	-0.00313	0.00783	0.00648	0.00236	0.0963	-1.77E-4	7.94	-4.68E-4	-0.107	-0.00827	0.00753	7.92E-4	-0.00622
11	-0.094	-0.0145	0.00409	-0.11	3.59E-4	-3.32E-4	0.00587	-3.26E-5	-0.0963	-4.68E-4	5.46	-0.00686	-0.0910	-0.00766	-0.00341	2.45E-4
12	-0.0603	-0.00409	-0.0184	-4.19E-4	2.8E-4	0.083	2.86E-4	0.00587	-0.00236	-0.107	-0.00686	4.66	-0.0846	1.44E-4	0.00766	-6.18E-4
13	-0.00261	-3.59E-4	2.8E-4	-0.00362	1.63E-5	0.00362	2.8E-4	3.59E-4	-0.00783	-0.00827	-0.091	-0.0846	1.67	-0.0846	0.0910	-0.00261
14	-6.18E-4	-0.00587	2.85E-4	-0.083	2.8E-4	4.19E-4	-0.0184	0.00409	0.00148	0.00753	-0.00766	1.44E-4	-0.0846	4.66	0.00686	-0.0603
15	-2.45E-4	-3.26E-5	-0.00587	-3.32E-4	-3.59E-4	-0.11	-0.00409	-0.0145	0.045	7.92E-4	-0.00341	0.00766	0.091	0.00686	5.46	0.0940
16	8.16E-6	0.00686	6.18E-4	0.00229	0.00261	0.00704	0.0603	0.094	-0.00253	-0.00622	2.45E-4	-6.18E-4	-0.00261	-0.0603	0.0940	0.00

S3. Schematic view of the one-electron pathways in Nap-Et-Nap and Nap-Et_U-Et_L-Nap

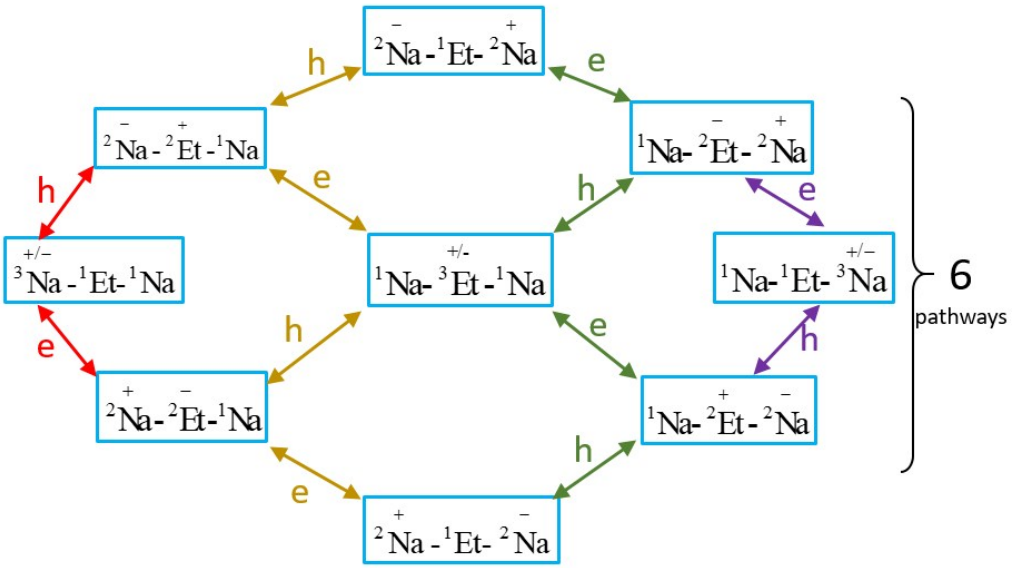

Figure S1. Map of the six one-electron pathways in Nap-Et-Nap. The "e" represents an electron transfer process from left to right, while "h" represents a hole transfer process from left to right.

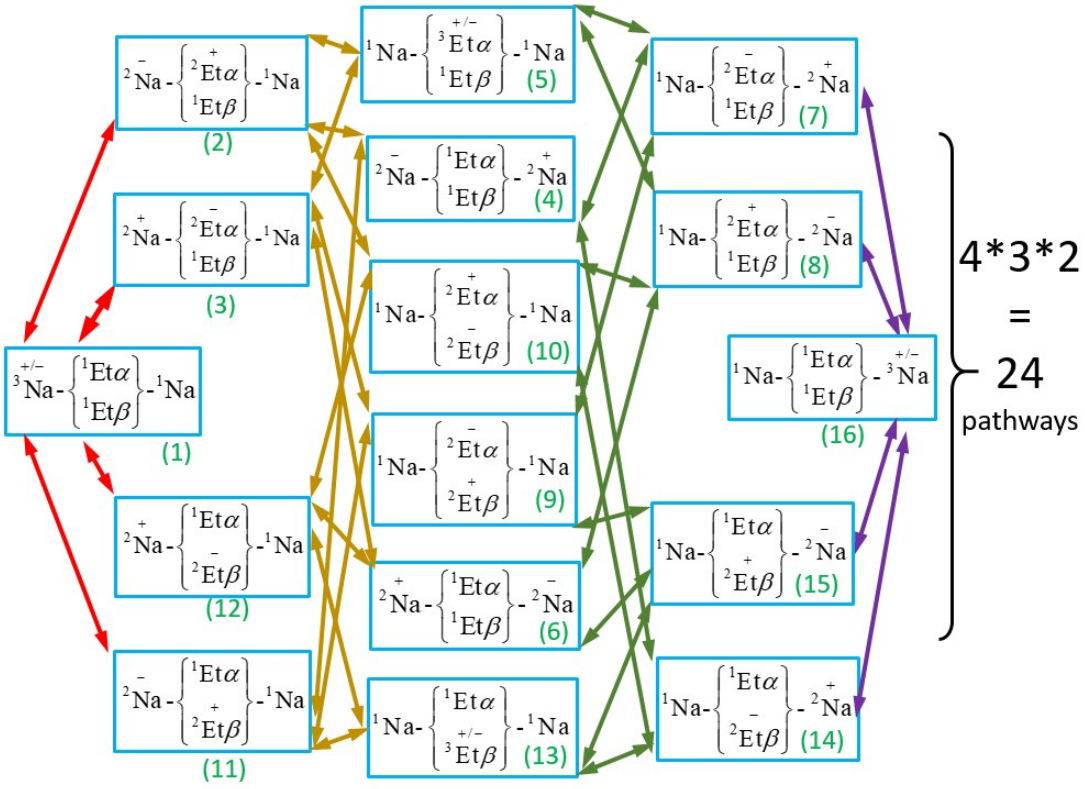

Figure S2. Map of the 24 one-electron pathways in Nap-Et_U-Et_L-Nap. The states are connected by electron or hole transfer in similar way as in Figure S1.

S4. The Dexter coupling in the naphthalene-naphthalene dimer based on FSD and CDFT-CI analysis

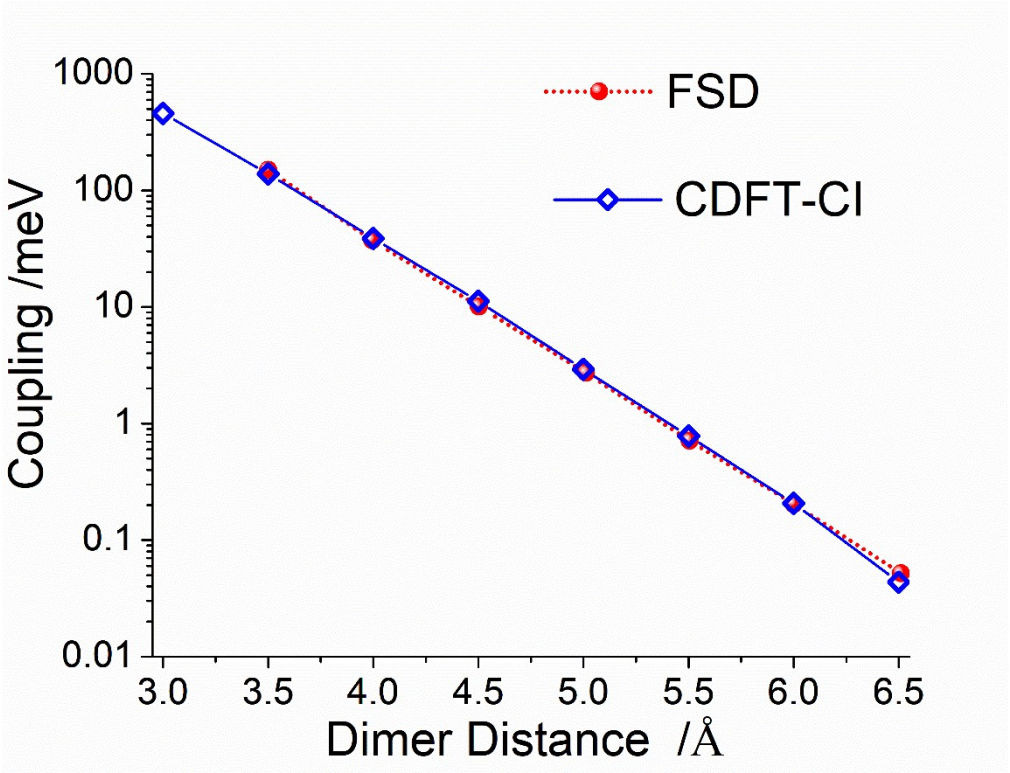

Figure S3. The Dexter triplet energy transfer coupling in the naphthalene-naphthalene dimer computed from the FSD method and from the CDFT-CI method. The dimer molecular geometry and results of the FSD method with a 6-311+G* basis set (red line) are taken from the study of You and Hsu.[1]

References

1. Z. Q. You and C. P. Hsu, *J. Chem. Phys.*, 2010, **133**, 074105.