

Supplementary Information to
Towards Direct Enzyme Wiring: a Theoretical Investigation of Charge
Carriers Transfer Mechanisms between Glucose Oxidase and Organic
Semiconductors

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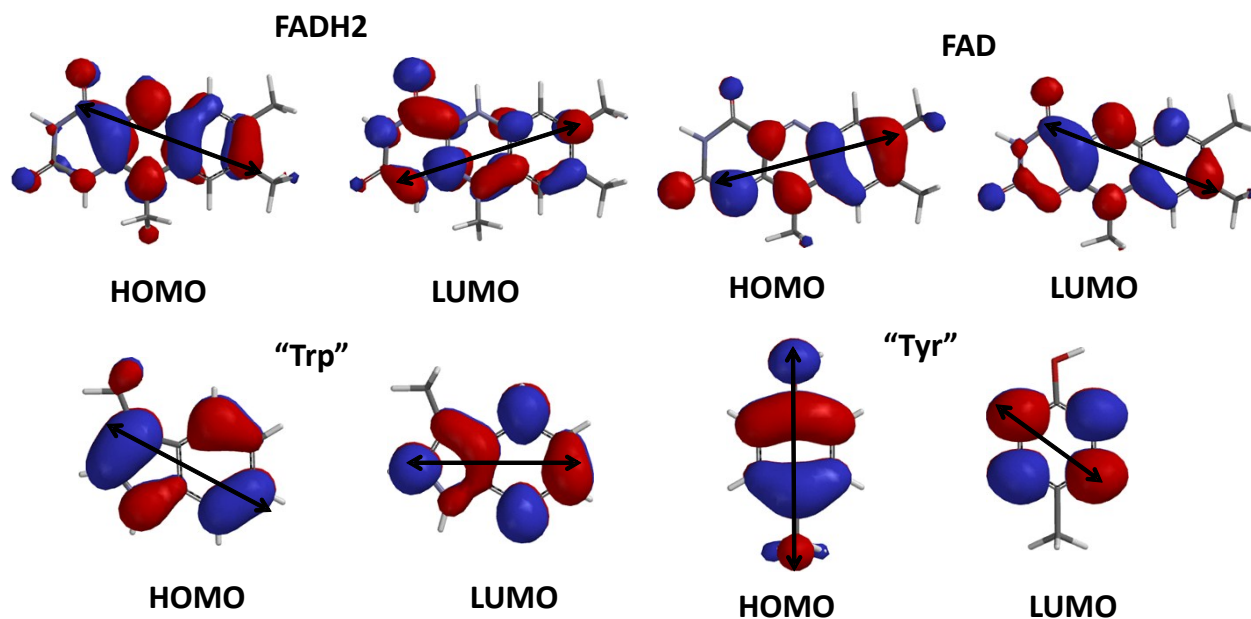


Figure S1. Oscillator (symmetry) vectors of HOMO and LUMO of the redox-able moieties.

Table S1. Orientation descriptors α and θ of redox-able moieties in enzyme.

Entry	Pathway	α from HOMO/ deg.	θ from HOMO/ deg	α from LUMO/ deg	θ from LUMO/ deg
1	FADH ₂ -Trp(426)	-12.1	148	-82.3	148
2	Trp(426)-Trp(122)	5.8	106	71.1	106
3	Trp(122)-Trp(131)	26.8	155	30.2	155
4	Trp(131) \rightarrow Tyr(139)	-111	117	163	117

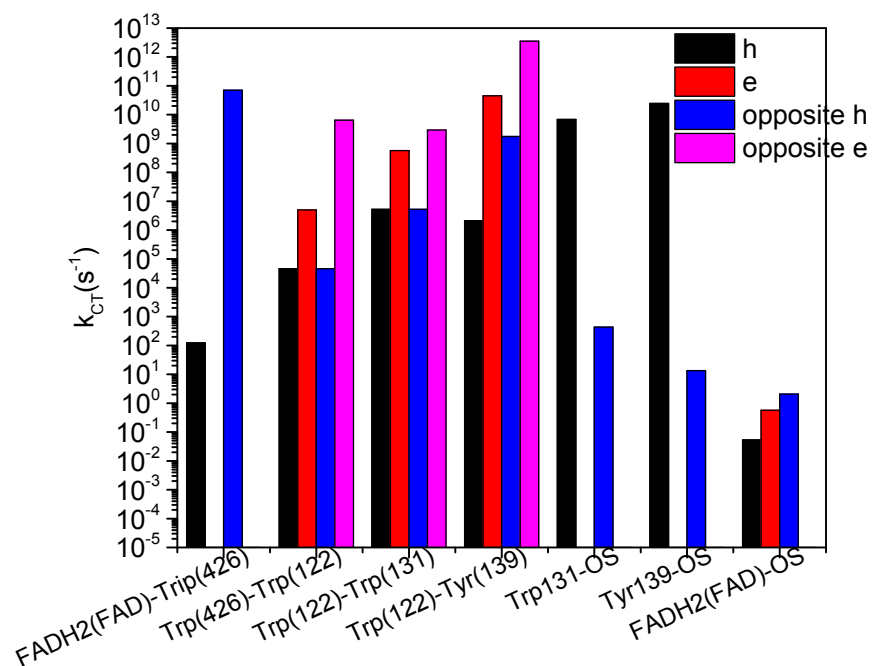


Figure S2. Rate constants calculated at optimal values of IP= 5 eV and EA = 4 eV.

Details of DFT computations

The geometries of redox-able residues were optimized by using the B3LYP functional and 6-31+G(d) basis set followed by calculations of their harmonic vibrational frequencies to verify their stability. All the calculated vibrational frequencies are real, which indicates the true minimum of total energy on a potential energy hypersurface. For the DFT calculations, the Spartan'14 software at temperature of 298 K was used.

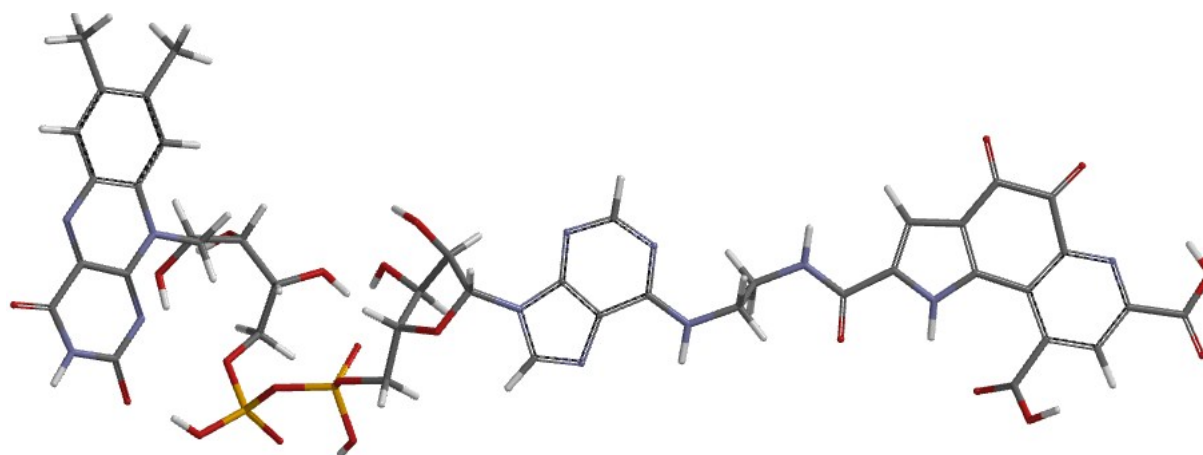


Figure S3. Optimised structure of Willner's covalently connected PQQ and flavin adenine dinucleotide adduct.

Coordinates

Coordinates of all calculated system with active FAD form:

C	-6.844229	-0.098872	-7.101192
C	-6.347474	-0.796525	-8.183479
C	-6.870139	-1.018608	-6.007693
N	-6.089705	-2.089944	-7.812871
C	-6.353058	-2.247279	-6.476829
C	-7.235411	-0.926532	-4.668871
C	-6.232798	-3.361934	-5.655920
C	-7.115142	-2.029716	-3.843791
C	-6.617181	-3.249933	-4.346452
C	9.320671	-0.459201	3.602480
C	9.549167	0.882097	3.464211
C	7.899712	-0.624748	3.663789
N	8.343811	1.559015	3.431500
C	7.325893	0.657698	3.544249
C	7.053613	-1.723872	3.798091
C	5.935306	0.870946	3.561045
C	5.678165	-1.526853	3.813703

C	5.141445	-0.227915	3.693331
C	8.410962	-6.258216	4.783605
C	8.828320	-7.033339	5.821421
C	6.976457	-6.235418	4.849338
N	7.744455	-7.530357	6.506302
C	6.593603	-7.064381	5.913911
C	5.983787	-5.641130	4.054570
C	5.261586	-7.294915	6.252563
C	4.659085	-5.873472	4.389073
C	4.306599	-6.689994	5.473795
C	8.361214	-3.394777	-6.438004
C	8.509065	-4.049505	-7.619977
C	7.111618	-2.694884	-6.522793
N	7.441460	-3.785900	-8.449251
C	6.581302	-2.933345	-7.801923
C	6.421407	-1.845855	-5.648866
C	5.379827	-2.372747	-8.236349
C	5.238676	-1.279691	-6.085450
C	4.724830	-1.545959	-7.358136
C	-11.398967	-9.104366	2.350063
C	-11.194220	-7.845250	1.877341
C	-10.363946	-9.915509	1.771450
N	-10.102662	-7.812380	1.048986
C	-9.576111	-9.075344	0.967587
C	-10.040872	-11.276536	1.860623
C	-8.467799	-9.542084	0.253174
C	-8.936101	-11.732558	1.163489
C	-8.168177	-10.871960	0.375628
C	12.788978	7.581519	-1.549803
C	13.578471	6.466756	-1.412578
C	11.645040	7.358986	-0.703667

N	13.003341	5.591922	-0.532686
C	11.823047	6.111170	-0.075951
C	10.501764	8.112235	-0.408438
C	10.886921	5.580941	0.809806
C	9.567543	7.569220	0.459019
C	9.774481	6.328466	1.082843
C	-7.364662	1.340869	-7.117271
H	-6.638903	1.986029	-7.625463
H	-7.505817	1.689830	-6.087942
H	-8.321828	1.377417	-7.649918
C	-12.511848	-9.572381	3.291562
H	-13.048125	-8.701188	3.684813
H	-12.073973	-10.137451	4.122331
H	-13.210128	-10.213544	2.741533
C	9.283395	-5.513950	3.769263
H	9.266129	-4.440654	3.990517
H	8.895327	-5.684916	2.758624
H	10.313280	-5.883481	3.832507
C	10.367471	-1.573189	3.687341
H	11.327979	-1.201240	3.312783
H	10.043734	-2.425796	3.079498
H	10.480073	-1.890006	4.730492
C	9.292385	-3.445793	-5.223805
H	9.983566	-2.595881	-5.257509
H	9.862861	-4.381481	-5.239964
H	8.697327	-3.396536	-4.304732
C	13.030406	8.812317	-2.427760
H	13.926326	9.339145	-2.079915
H	12.165052	9.481891	-2.364131
H	13.172673	8.497010	-3.467740
H	-6.184502	-0.380323	-9.184196

H	-7.618080	0.019152	-4.268295
H	-7.409171	-1.955325	-2.790591
H	-6.537061	-4.117713	-3.681806
H	-5.839960	-4.307467	-6.046896
H	8.234461	2.560821	3.338912
H	5.509605	1.876927	3.471625
H	4.053130	-0.099038	3.706648
H	5.006129	-2.386062	3.920208
H	7.468995	-2.733888	3.890506
H	10.350283	9.103356	-0.851100
H	8.643643	8.122270	0.663372
H	9.034094	5.953609	1.798753
H	11.036952	4.598493	1.271869
H	14.529581	6.302161	-1.931727
H	10.537721	1.349586	3.390509
H	3.867308	-5.407705	3.791271
H	3.246872	-6.848273	5.704322
H	4.988707	-7.930702	7.102580
H	6.248055	-5.012939	3.196226
H	9.875937	-7.232471	6.074525
H	7.786486	-8.139066	7.313675
H	13.391398	4.697601	-0.261120
H	-10.646627	-11.960631	2.465843
H	-8.657903	-12.790521	1.230843
H	-7.300377	-11.273317	-0.160144
H	-7.867491	-8.874225	-0.375166
H	-11.816039	-6.977262	2.124639
H	-9.745013	-6.992204	0.576183
H	4.690173	-0.605534	-5.417712
H	6.808847	-1.635930	-4.645354
H	3.778131	-1.084318	-7.661230

H	4.977228	-2.583064	-9.233794
H	7.312313	-4.158712	-9.381172
H	9.356820	-4.695044	-7.876507
H	-5.755784	-2.818213	-8.431148
H	-8.307879	6.699252	4.945587
C	-8.858794	7.309366	4.240370
C	-10.304815	8.908823	2.478559
C	-8.661877	7.145021	2.859433
C	-9.757841	8.251778	4.733648
C	-10.500366	9.073612	3.838838
C	-9.399867	7.960396	1.962937
H	-10.846470	9.509880	1.755181
N	-7.774637	6.217725	2.333211
N	-9.260956	7.854760	0.604311
C	-8.422479	6.978518	0.138989
C	-8.267004	6.857152	-1.347703
O	-8.879987	7.526717	-2.158175
N	-7.344359	5.894028	-1.705840
H	-7.189369	5.759264	-2.698129
C	-6.579850	5.061624	-0.853641
O	-5.806120	4.263059	-1.347503
C	-7.606785	6.087289	0.964167
C	-6.994412	5.355034	3.228218
H	-6.363939	5.966716	3.879097
H	-6.375431	4.713922	2.605968
N	-6.757889	5.204603	0.511865
C	-11.477747	10.100286	4.354285
H	-11.951797	10.634877	3.528044
H	-12.272406	9.640811	4.954038
H	-10.987696	10.843390	4.994721
C	-9.937255	8.394274	6.223597

H	-9.691869	9.408152	6.560700
H	-10.976158	8.208666	6.520847
H	-9.301214	7.694671	6.770544
H	-7.667254	4.747581	3.839420

Coordinates of all calculated system with the active FADH₂ form:

C	-6.782349	-0.148537	-7.173393
C	-6.280832	-0.857475	-8.246108
C	-6.816053	-1.057637	-6.071247
N	-6.027505	-2.147717	-7.861618
C	-6.298608	-2.291692	-6.525619
C	-7.188631	-0.952007	-4.735443
C	-6.184977	-3.398591	-5.693349
C	-7.074995	-2.047395	-3.899113
C	-6.576467	-3.273285	-4.387196
C	9.321796	-0.434343	3.623702
C	9.553515	0.905150	3.473802
C	7.900216	-0.596768	3.678637
N	8.349601	1.583862	3.427814
C	7.329422	0.685483	3.543533
C	7.051369	-1.693041	3.818775
C	5.939155	0.901353	3.550478
C	5.676219	-1.493438	3.824778
C	5.142558	-0.194769	3.688891
C	8.394889	-6.220074	4.855517
C	8.805021	-6.985894	5.903075
C	6.960082	-6.194095	4.912985
N	7.716438	-7.474358	6.586625
C	6.569769	-7.012072	5.983330
C	5.972959	-5.605737	4.106977
C	5.235460	-7.236964	6.316715

C	4.645986	-5.832489	4.436270
C	4.285949	-6.637885	5.526815
C	8.413093	-3.464897	-6.393259
C	8.566348	-4.131254	-7.568022
C	7.165273	-2.763635	-6.491789
N	7.503878	-3.873762	-8.405769
C	6.641678	-3.013478	-7.771515
C	6.471744	-1.904994	-5.629965
C	5.443678	-2.454962	-8.218050
C	5.292510	-1.340966	-6.078605
C	4.785297	-1.618582	-7.351527
C	-11.406307	-9.054367	2.338494
C	-11.196618	-7.800233	1.854820
C	-10.369555	-9.872889	1.773532
N	-10.100389	-7.777293	1.032318
C	-9.575704	-9.041915	0.966043
C	-10.049476	-11.233564	1.877622
C	-8.464273	-9.517491	0.262382
C	-8.941663	-11.698250	1.191117
C	-8.167774	-10.846655	0.399320
C	12.833552	7.550144	-1.586276
C	13.620225	6.435357	-1.433895
C	11.684498	7.337814	-0.744461
N	13.038586	5.570070	-0.548854
C	11.856710	6.095795	-0.103766
C	10.540971	8.095904	-0.462916
C	10.914680	5.575796	0.781796
C	9.600924	7.562940	0.404481
C	9.802101	6.327893	1.041379
C	-7.300048	1.291904	-7.206257
H	-6.570281	1.930844	-7.716564

H	-7.446314	1.651025	-6.181145
H	-8.254154	1.325014	-7.744589
C	-12.525288	-9.511304	3.278203
H	-13.062158	-8.635408	3.660032
H	-12.093096	-10.069113	4.116819
H	-13.221655	-10.156499	2.730471
C	9.274337	-5.487175	3.838958
H	9.257800	-4.411766	4.049763
H	8.891611	-5.667190	2.827854
H	10.303175	-5.857908	3.911531
C	10.366064	-1.549320	3.725157
H	11.329330	-1.182706	3.352423
H	10.044170	-2.407172	3.123750
H	10.472255	-1.856262	4.771927
C	9.337369	-3.505855	-5.173423
H	10.030282	-2.657538	-5.211437
H	9.906212	-4.442668	-5.177370
H	8.737275	-3.446682	-4.258217
C	13.082135	8.771989	-2.474682
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H	13.229634	8.446415	-3.510762
H	-6.111508	-0.451233	-9.249857
H	-7.571802	-0.001826	-4.346146
H	-7.374769	-1.962329	-2.848343
H	-6.501650	-4.134756	-3.713783
H	-5.791692	-4.348546	-6.072991
H	8.242604	2.584921	3.324969
H	5.515803	1.907180	3.448987
H	4.054423	-0.063837	3.694865
H	5.002026	-2.350385	3.935786

H	7.464379	-2.702855	3.923242
H	10.393780	9.082978	-0.915947
H	8.676910	8.119575	0.598315
H	9.057041	5.961273	1.756705
H	11.060328	4.597584	1.254135
H	14.573918	6.264073	-1.946094
H	10.543319	1.370150	3.401142
H	3.858416	-5.371103	3.829581
H	3.224662	-6.792051	5.752912
H	4.956672	-7.864038	7.171274
H	6.243169	-4.986323	3.244115
H	9.850841	-7.184436	6.163954
H	7.752842	-8.075327	7.400047
H	13.423481	4.677723	-0.266515
H	-10.659855	-11.910714	2.485998
H	-8.665783	-12.756007	1.270218
H	-7.297730	-11.254701	-0.127688
H	-7.859242	-8.856790	-0.368987
H	-11.818219	-6.928799	2.090255
H	-9.738603	-6.962351	0.553648
H	4.741519	-0.659429	-5.420478
H	6.853954	-1.686090	-4.626365
H	3.841153	-1.158204	-7.664356
H	5.046275	-2.674172	-9.215664
H	7.379259	-4.255314	-9.334764
H	9.414341	-4.780741	-7.813565
H	-5.691468	-2.882506	-8.470969
H	-8.362014	6.873910	4.880938
C	-8.947873	7.399457	4.134015
C	-10.397711	8.789822	2.238006
C	-8.886801	6.996704	2.804061

C	-9.750832	8.475588	4.547547
C	-10.489117	9.178142	3.581931
C	-9.616917	7.710950	1.831070
H	-10.962164	9.334501	1.484978
N	-8.109263	5.870463	2.380636
C	-7.955630	6.623737	-1.246456
O	-8.499554	7.279361	-2.132561
N	-6.832012	5.815401	-1.517674
H	-6.495560	5.817421	-2.472102
C	-6.091536	5.074971	-0.617899
O	-5.094239	4.434061	-0.903066
C	-7.607036	4.914007	3.348132
H	-8.379065	4.732478	4.099635
H	-7.402950	3.960677	2.854056
N	-6.591914	5.128627	0.683426
H	-6.003343	4.682763	1.370470
C	-7.704624	5.861909	1.057374
C	-8.393032	6.575825	0.121214
N	-9.555230	7.282776	0.497572
H	-9.849449	7.940582	-0.214920
C	-11.369060	10.342551	3.967600
H	-12.149104	10.043295	4.678360
H	-11.864561	10.770787	3.092537
H	-10.794742	11.143181	4.449600
C	-9.803649	8.859313	6.007322
H	-10.820490	8.784742	6.412236
H	-9.476746	9.893899	6.168410
H	-9.160366	8.212478	6.610238
H	-6.696715	5.251080	3.866637