

# Supporting Information

## Spectroscopic and Electronic Structure Study of the Enzyme-Substrate Complex of Intradiol Dioxygenases: Substrate Activation by a High Spin Ferric Non-Heme Iron Site

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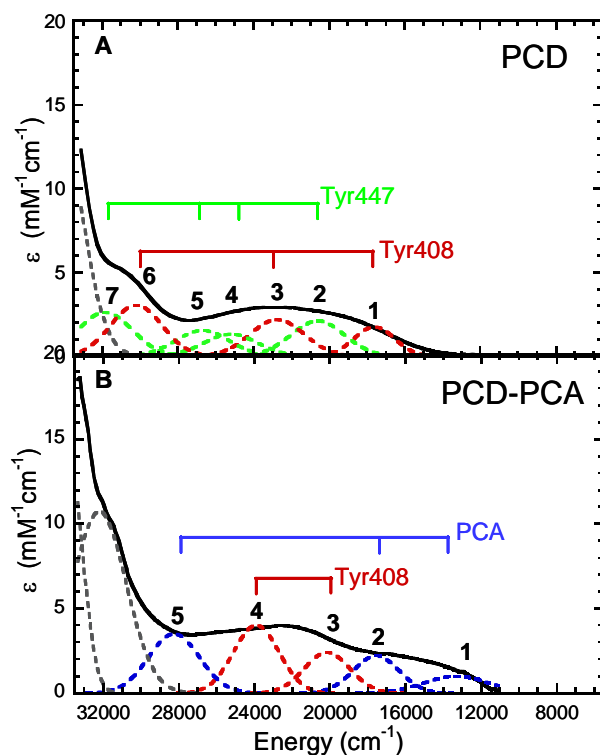
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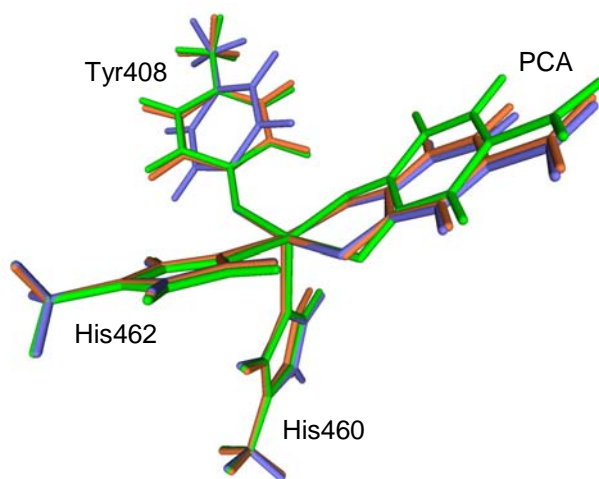
**Table S1.** Cartesian coordinates of PCD-PCA model optimized with Gaussian BP86 and LanL2DZ as basis set

Fe	3.153799	-0.396921	-0.092229
O	4.910209	0.264824	-0.416268
C	5.538830	1.385579	-0.905698
C	6.850401	1.282774	-1.457662
C	7.487417	2.422915	-2.000026
C	6.850649	3.693235	-2.006299
C	5.555158	3.787680	-1.425625
C	4.902708	2.665340	-0.882744
C	7.496111	4.912735	-2.645815
H	7.344358	0.303476	-1.468238
H	8.491048	2.321801	-2.435231
H	8.571124	4.748354	-2.843876
H	7.015247	5.159263	-3.613802
H	7.403194	5.807760	-2.001317
H	5.042459	4.759604	-1.415865
H	3.888622	2.729154	-0.474971
N	3.688235	-2.317116	-0.928221
C	2.896297	-3.234967	-1.525813
N	3.664878	-4.307519	-1.953185
C	5.019521	-4.070667	-1.612723
C	5.006886	-2.822511	-0.981664
C	6.138150	-5.045851	-1.918085
H	1.822556	-3.131601	-1.662323
H	3.313853	-5.118289	-2.464058
H	5.832410	-2.232254	-0.592929
H	6.241548	-5.224152	-3.005216
H	5.979804	-6.023442	-1.423796
H	7.093387	-4.633471	-1.554668
N	3.443059	-0.978068	1.913149
C	3.610648	-0.174270	2.980075
N	3.881061	-0.939730	4.105041
C	3.886219	-2.301701	3.735117
C	3.610844	-2.299215	2.367454
C	4.170666	-3.429599	4.684489
H	3.558962	0.910826	2.964727
H	4.070669	-0.575307	5.039202
H	3.573222	-3.139990	1.679590
H	4.111260	-4.390386	4.147200
H	5.185903	-3.356569	5.119322
H	3.448561	-3.466771	5.522943
O	2.253424	1.392519	-0.151229
O	1.083311	-0.949608	-0.187433
C	1.024704	1.379485	-0.742430
C	0.371241	0.089187	-0.799606
C	-0.869613	-0.055820	-1.443270
C	-1.487873	1.081257	-2.035055
C	-0.856369	2.359041	-1.962273
C	0.393161	2.514230	-1.327804
C	-2.824574	0.916504	-2.743324
O	-3.134272	-0.313201	-3.075074
O	-3.548352	1.972754	-2.944609
H	-1.362004	-1.028949	-1.544758
H	-1.367660	3.207168	-2.430902

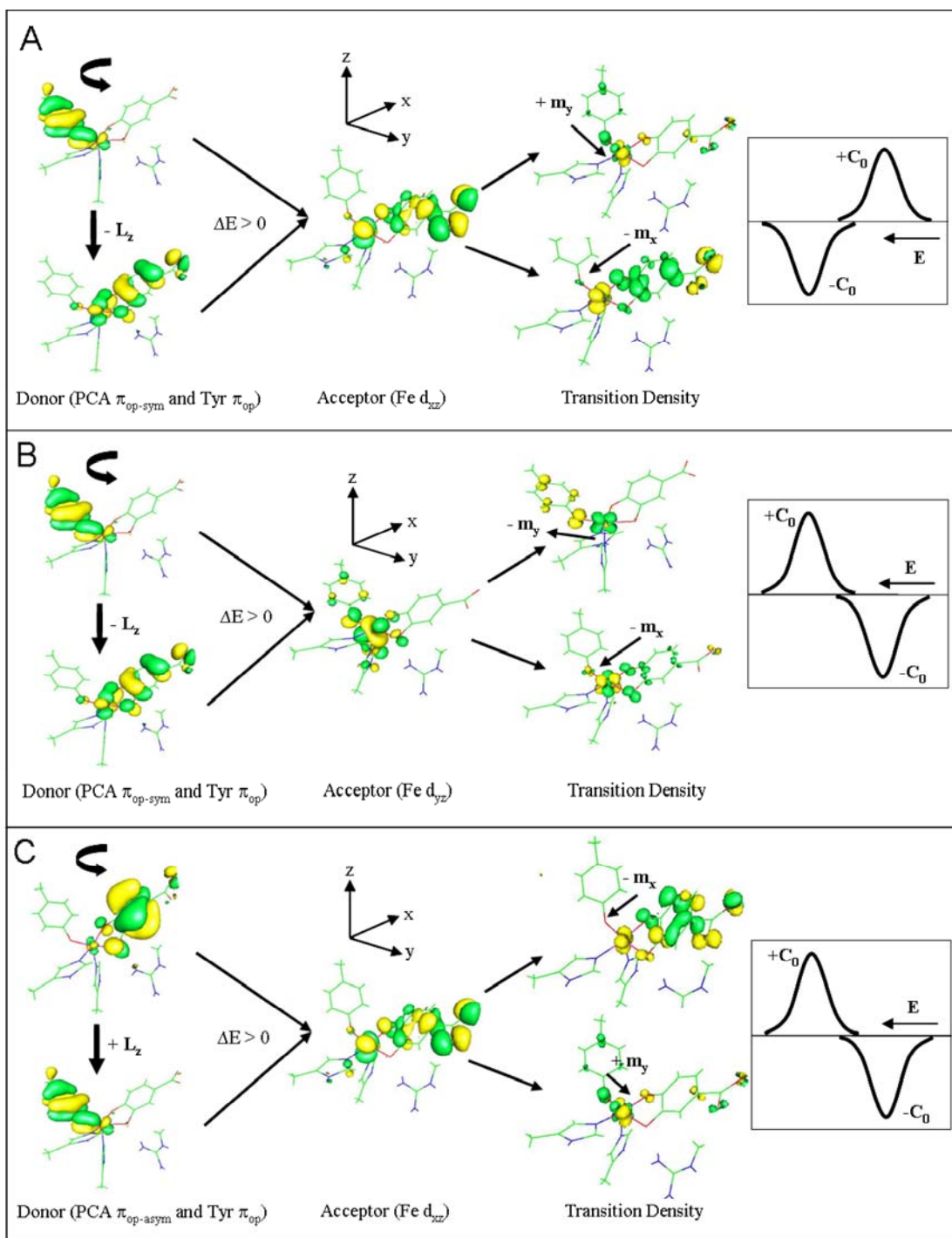
H	0.907047	3.481914	-1.297516
O	-4.853903	-2.081642	-3.498131
C	-5.942608	-2.111673	-2.656224
C	-6.456755	-3.386942	-2.408135
C	-7.577110	-3.529495	-1.592559
C	-8.160085	-2.433463	-0.984183
C	-7.601487	-1.169157	-1.217557
C	-6.512092	-0.996452	-2.055972
C	-9.333103	-2.640931	-0.057484
H	-4.248230	-1.228269	-3.403276
H	-5.974803	-4.241316	-2.894317
H	-7.994060	-4.532317	-1.419437
H	-8.079526	-0.288513	-0.766091
H	-6.106736	-0.006916	-2.282773
H	-10.104626	-3.293012	-0.512191
H	-9.027692	-3.123069	0.894837
H	-9.824110	-1.684951	0.205516
N	0.209634	-1.701048	2.101788
N	-0.917180	-2.859871	3.727433
C	-0.751378	-1.713943	3.013267
N	-1.476095	-0.664187	3.306149
C	-1.505051	0.685734	2.857176
H	0.405338	-1.172942	1.150376
H	0.915757	-2.439978	2.188493
H	-0.667471	-3.753443	3.310628
H	-1.409293	-2.878949	4.619249
H	-2.319270	-0.896238	3.845155
H	-0.539424	0.974542	2.408001
H	-2.281864	0.852894	2.088922
H	-1.708711	1.366122	3.701086
C	-4.537363	2.961220	-0.057782
C	-5.397954	1.887051	-0.245855
C	-5.842138	1.136785	0.846162
C	-5.467441	1.415802	2.150695
C	-4.633989	2.518206	2.327645
C	-4.145997	3.275017	1.243335
C	-3.298509	4.294796	1.785908
C	-3.278256	4.090285	3.158100
N	-4.088201	3.019935	3.480782
C	-2.555486	5.333990	1.003442
H	-4.150706	3.499891	-0.928493
H	-5.683860	1.619092	-1.263914
H	-6.486178	0.271369	0.658314
H	-5.838721	0.815992	2.991745
H	-4.368318	2.758351	4.423461
H	-2.764961	4.668430	3.926719
H	-1.965196	5.999093	1.659972
H	-1.859515	4.870871	0.277010
H	-3.249546	5.969987	0.419628



**Figure S1.** Gaussian resolution (---) of UV/VIS Abs spectra (—) at 4°C (A) PCD; red: Tyr408  $\rightarrow$  Fe<sup>3+</sup> CT, green: Tyr447  $\rightarrow$  Fe<sup>3+</sup> CT, (B) PCD-PCA; blue: PCA  $\rightarrow$  Fe<sup>3+</sup> CT, red: Tyr408  $\rightarrow$  Fe<sup>3+</sup> CT.



**Figure S2.** Overlay of PCD-PCA models optimized with BP86/LanL2DZ (green), BP86 + 10% HF exchange / TZVP (orange) and BP86 + 10% HF exchange / 6-31G\*/3-21G\* (purple). 2nd sphere residues not presented in diagram for clarity purpose.



**Figure S3.** Graphical prediction of the signs of the  $C_0$ -parameters (= signs of C-terms) of the Tyr and PCA  $\rightarrow$  Fe<sup>3+</sup> CT transitions.

**Complete Reference for the Gaussian 03 program package in Ref 43:**

Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J., J. A.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A., *Gaussian 03, Revision C.02*, <http://www.gaussian.com>, Wallingford CT, **2004**.