Supporting Information

Spectroscopic and Theoretical Investigation of Early Intermediates in Biomimetic Hydrogenase Catalyst [Fe$_2$(bdt)(CO)$_6$]

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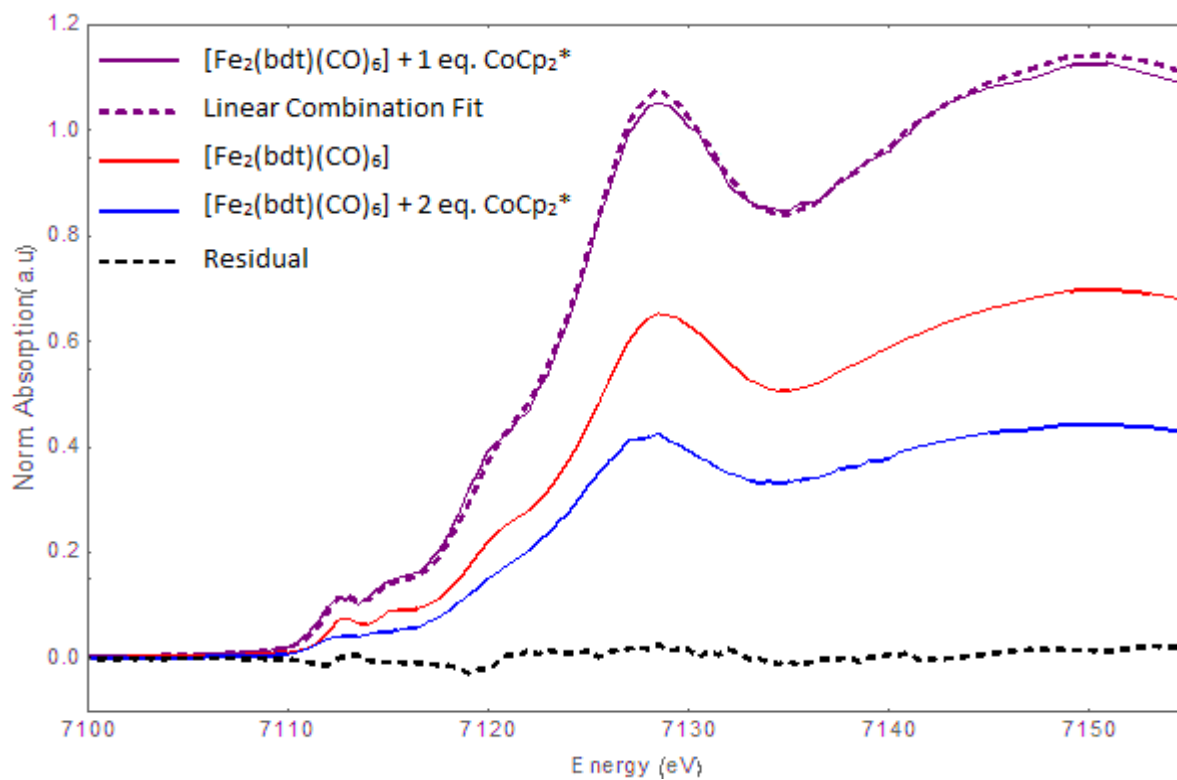
1. XANES analysis

Figure 1. Linear Combination fitting of the XANES region of [Fe₂(bdt)(CO)₆] with 1 eq. of reducing agent CoCp₂* with the standards [Fe₂(bdt)(CO)₆] and [Fe₂(bdt)CO₆] with 2 eq CoCp₂*.

Standard	Weight (error)	
[Fe₂(bdt)(CO)₆] + Precursor	0.604	(0.038)
[Fe₂(bdt)(CO)₆] 2eq. CoCp₂*	0.396 +	(0.044)
Sum	1.000	

Linear combination fit of [Fe2(bdt)CO6] with 1 eq CoCp₂* as flattened μ(E) from 7104.5 to 7154.5 eV.
Weights forced between 0 and 1 with no overall E_0 shift.
R-factor = 0.0008029 Reduced chi-square = 0.0001356.

2. EXAFS analysis

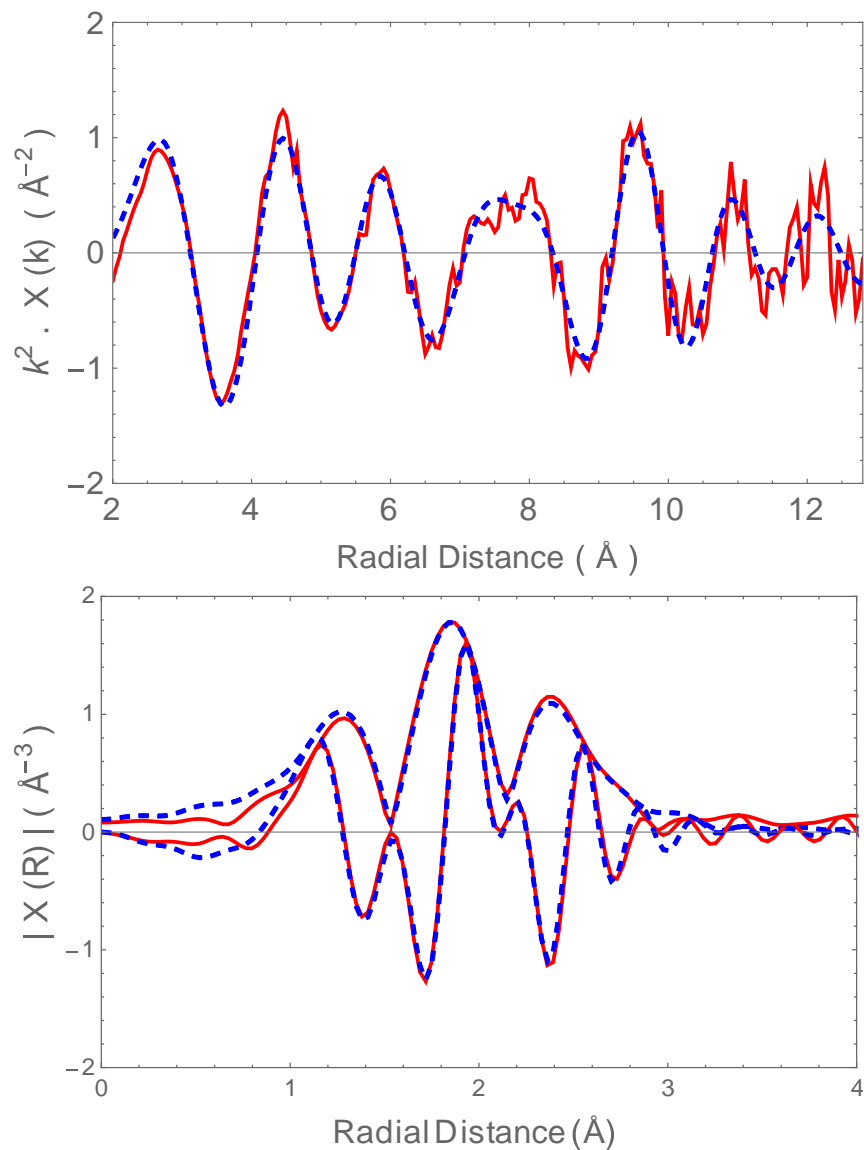**Figure 2. (Top)** k^2-weighted Fe K-edge EXAFS data of [Fe$_2$(bdt)(CO)$_6$] with 1 eq. of reducing agent CoCp$_2$* with the corresponding fit. **(Bottom)** k^2-weighted Fourier Transforms of the EXAFS data for 2 < k < 12 Å of [1] (left) and [1]$^{2-}$ (right). In all plots the data are represented by the solid lines (red), whereas the corresponding fits are the dotted lines (blue).

Table 1. Fe K-edge EXAFS fitting parameters for [Fe$_2$(bdt)(CO)$_6$] with 1eq. CoCp$_2$*, where N = coordination number, σ^2 = Debye Waller factor [Å^{-2}], R = fitted bond length [Å].

Sample	Shell	N	σ^2	R_{fit} (Å)
[Fe$_2$(bdt)(CO)$_6$ + 1 eq. CoCp$_2$*][a]	Fe - C	2.5	0.001(1)	1.79(1)
	Fe - S	1.75	0.003(3)	2.28(2)
	Fe - Fe	1.0	0.004(4)	2.45(3)
	Fe - O	3.0	0.002(5)	2.97(6)
	Fe - CO	5.5	0.001(3)	2.97(6)
	Fe - COC	2.5	0.003(3)	2.97(6)

[a]**k range = 2 – 12 Å, R range = 1 – 3.2 Å; k-weighted fit = 1,2,3 E$_0$ = -2.6(8) eV, S$_0^2$ = 0.90. R-factor fit: 0.0188, * fixed value**

2. Computational Methods

All geometry optimizations and IR calculations were conducted using ADF[1,2] with the TZ2P basis set and BP86[3] or OPBE[4] functional. COSMO solvent models were carried out employing acetonitrile.[5] Transition States were located using a linear transit method,[6] all validated by one single negative infrared frequency. TD-DFT XANES calculations were performed with a 50 Davidson excitation restriction window where only singlet Quadrupole and Dipole Allowed transitions are selected from the irons 1s orbitals.[7,8] In all TD-DFT calculations, B3LYP − d3 and a QZ4P Slater-type basis set was applied.[9] The intensities include second-order contributions due to the magnetic-dipole and electric-quadrupole transition moments.[10] The spectra were shifted by 151.0 eV for comparison to experiment. These shifts are chosen such that the energy of the first peak in the calculated spectrum agrees with the first peak in the experimental spectrum. While these shifts are rather large, they do not affect the relative position of the peaks.[11]

Iron K-Edge XANES spectra were simulated with FEFF9.[12,13] These XANES calculations were carried out using both the crystallographic and DFT geometry optimized coordinates. In all cases a Hedin−Lundqvist potential was utilized.[14] The many-body reduction factor (S_0^2) was kept at 1.0. The default core-hole broadening (1/3 of the energy step) was utilized for spectral plots, with no additional experimental broadening.

3. Coordinates of calculated structures

All coordinates are shown for OPBE basis set in combination with a (Acetonitrile) COSMO solvent model.
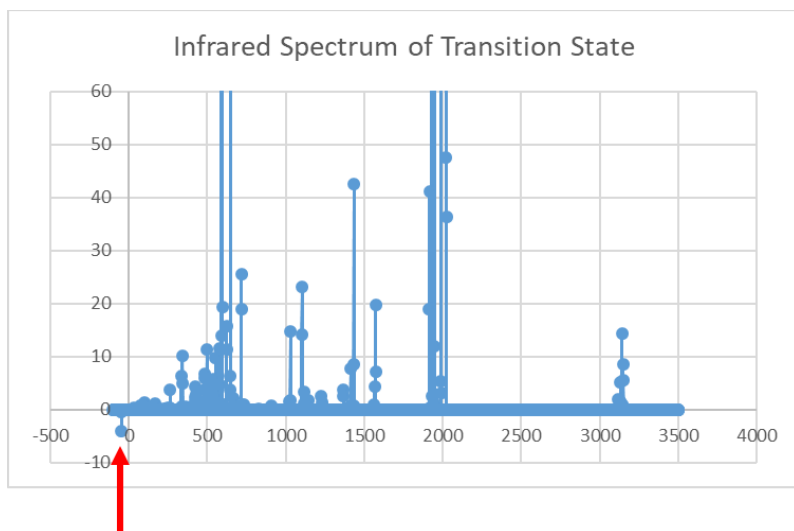
[Fe₂(bdt)(CO)₆]

	ATOMS	X	Y	Z	Angstroms
1	Fe	2.2329	0.4814	3.5393	
2	Fe	4.1595	1.3408	2.2345	
3	S	2.5512	2.6846	3.087	
4	S	2.3452	0.3795	1.2736	
5	C	2.7498	0.7886	5.2143	
6	O	3.104	1.0115	6.271	
7	C	2.6567	-1.2537	3.62	
8	O	2.9111	-2.3612	3.6512	
9	C	5.3078	1.9108	3.4735	
10	O	6.0382	2.2416	4.2706	
11	C	5.1218	-0.1654	2.0661	
12	O	5.7504	-1.1149	2.0142	
13	C	0.4463	0.3795	3.785	
14	O	-0.6657	0.2865	3.9407	
15	C	4.7678	2.2815	0.8283	
16	O	5.1288	2.8486	-0.0877	
17	C	1.4817	2.8958	1.6854	
18	C	1.3743	1.806	0.8444	
19	C	0.5414	1.8695	-0.2584	
20	C	-0.1667	3.0184	-0.496	
21	C	-0.0678	4.086	0.323	
22	C	0.7708	4.0388	1.4489	
23	H	0.4639	1.1415	-0.8317	

[Fe₂(bdt)µ-CO(CO)₅]¹⁻

	ATOMS	X	Y	Z	(Angstroms)
1	Fe	0.834037	0.023193	-1.00743	
2	Fe	1.167058	-2.29226	0.053163	
3	S	0.108713	-0.57673	1.001072	
4	S	2.79997	0.647337	0.003807	
5	C	2.400376	0.735745	1.687844	
6	C	1.181175	0.213777	2.151631	
7	C	0.834658	0.287334	3.502795	
8	C	1.710948	0.867746	4.414175	
9	C	2.934241	1.373512	3.96673	
10	C	3.278864	1.31246	2.621831	
11	C	-0.54263	-0.73363	-1.75367	
12	C	1.731968	-0.0783	-2.50021	
13	C	0.264122	1.664374	-1.12867	
14	C	1.986239	-3.12715	1.344653	
15	C	-0.09995	-3.48926	-0.12497	
16	C	2.126662	-2.86696	-1.28828	
17	O	-1.46783	-1.17215	-2.30082	
18	O	2.305901	-0.09823	-3.5079	
19	O	-0.13689	2.745434	-1.25798	
20	O	2.523883	-3.76208	2.163887	
21	O	-0.8631	-4.36655	-0.23088	
22	O	2.746668	-3.35886	-2.14671	
23	H	-0.12044	-0.11686	3.836388	
24	H	1.440698	0.928609	5.467023	
25	H	3.624496	1.833652	4.673417	
26	H	4.229504	1.721203	2.282368	

Transition state from [Fe₂(bdt)(CO)₆]¹⁻ → [Fe₂(bdt)μ-CO(CO)₅]¹⁻

	ATOMS	X	Y	Z	(Angstroms)
1	Fe	0.544273	0.088842	-0.90344	
2	Fe	1.477808	-2.15455	-0.12212	
3	S	0.026865	-0.75849	1.117265	
4	S	2.627281	0.398829	0.034342	
5	C	2.291953	0.612849	1.731562	
6	C	1.096633	0.078751	2.243475	
7	C	0.801639	0.180283	3.601973	
8	C	1.69106	0.822831	4.462863	
9	C	2.883746	1.345544	3.962019	
10	C	3.188284	1.2367	2.607054	
11	C	-1.12069	-0.03787	-1.42673	
12	C	1.136174	-0.89046	-2.26096	
13	C	0.620422	1.74387	-1.45488	
14	C	2.052514	-2.99364	1.305767	
15	C	0.293844	-3.39905	-0.63672	
16	C	2.839354	-2.74425	-1.10409	
17	O	-2.22763	-0.08125	-1.79093	
18	O	1.342836	-1.26512	-3.3525	
19	O	0.67719	2.838119	-1.86108	
20	O	2.417627	-3.61262	2.225118	
21	O	-0.34382	-4.31775	-0.97024	
22	O	3.711073	-3.2593	-1.68368	
23	H	-0.12644	-0.2451	3.982482	
24	H	1.450497	0.914467	5.521869	
25	H	3.582224	1.851184	4.629437	
26	H	4.118494	1.64825	2.217035	

Infrared Spectrum of Transition State

[Fe₂(bdt)(CO)₆]¹⁻

	ATOMS	X	Y	Z	(Angstroms)
1	Fe	0.247387	0.798281	1.578172	
2	Fe	0.018122	-1.48473	0.346721	
3	S	0.825926	0.523666	-0.59419	
4	S	-1.83904	1.230572	0.890531	
5	C	-0.52044	1.213856	-1.51657	
6	C	-2.69514	2.210773	-2.9429	
7	C	-1.72709	1.476586	-0.84304	
8	C	-0.40033	1.459832	-2.885	
9	C	-1.48396	1.967746	-3.60056	
10	C	-2.81976	1.957504	-1.57965	
11	H	0.558873	1.245292	-3.38541	
12	H	-1.38495	2.171586	-4.67887	
13	H	-3.77005	2.147881	-1.05341	
14	H	-3.558	2.606461	-3.50367	
15	C	1.660705	1.77247	1.90839	
16	O	2.59369	2.437766	2.132743	
17	C	-0.30951	0.907113	3.237574	
18	O	-0.65808	0.992134	4.347754	
19	C	1.1022	-0.85418	1.916489	
20	O	1.853356	-1.33779	2.700516	
21	C	-0.73452	-2.59835	1.492493	
22	O	-1.20551	-3.37518	2.222125	
23	C	-1.2852	-1.69805	-0.88959	
24	O	-2.09661	-1.97151	-1.67546	
25	C	1.260417	-2.59617	-0.24545	
26	O	2.035212	-3.38617	-0.61407	

[Fe₂(bdt)μ-CO(CO)₅]²⁻

	ATOMS	X	Y	Z	(Angstroms)
1	Fe	0.2028	0.0665	0.5594	
2	Fe	2.582	-0.1034	-0.4246	
3	S	1.6359	1.9626	-0.1182	
4	S	1.9621	0.0453	-2.6526	
5	C	1.2402	2.5373	-1.7214	
6	C	0.4012	3.4248	-4.2824	
7	C	1.2199	1.6522	-2.837	
8	C	0.8323	3.8659	-1.9297	
9	C	0.4266	4.3167	-3.1828	
10	C	0.7897	2.1013	-4.09	
11	H	0.8348	4.5489	-1.0615	
12	H	0.121	5.3696	-3.3141	
13	H	0.7752	1.3845	-4.9308	
14	H	0.0653	3.7652	-5.277	
15	C	-0.9608	0.1895	-0.8193	
16	O	-1.852	0.1267	-1.5847	
17	C	-0.319	-1.561	0.9284	
18	O	-0.7299	-2.6228	1.2377	
19	C	-0.5292	0.9254	1.9117	
20	O	-1.108	1.3855	2.8335	
21	C	2.9254	-1.8157	-0.5284	
22	O	3.2153	-2.9579	-0.5761	
23	C	4.2358	0.3858	-0.1702	
24	O	5.3661	0.6576	0.0477	
25	C	1.9401	-0.4311	1.3503	
26	O	2.3793	-0.8293	2.3933	

4. Redox potentials

Redox potentials were determined using the Born–Haber cycle approach[15], seen in scheme 1. By applying formula 1, the change in free energy of the redox process in solution can be obtained.[16] Now by the use of formula 2, the standard absolute redox potential (E^0) can be calculated, where F is the Faraday constant (23.061 kcal per volt gram equivalent) and Z equals 1.0 (one-electron redox processes).[16]
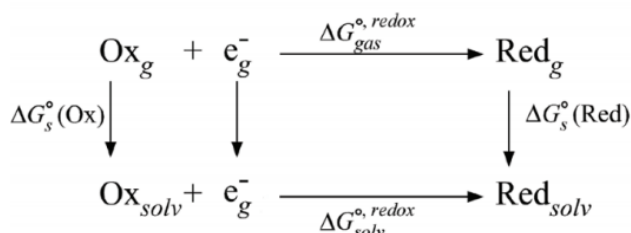
Scheme 1. Born Haber Cycle used for the calculation of redox potentials

$$E^0 = \frac{-\Delta G^o(soln,\ redox)}{ZF} \tag{1}$$

$$-\Delta G^o(soln,\ redox) = \Delta G^o(gas,\ redox) + \Delta G^o(solv, [Fe_2(bdt)(CO)_6]^{-1}) - \Delta G^o(solv,\ [Fe_2(bdt)(CO)_6]) \tag{2}$$

The tables below show the calculated parameters needed for the redox potentials. Table 2 gives the results in case of OPBE as basis set whereas table 3 represents the calculated parameters using BP86 as basis set.

Table 2. Redox parameters calculated using an OPBE basis set.

Starting product	Final product	ΔG^o (gas, redox) (kcal/mol)	ΔG^o (solution, redox) (kcal/mol)	ΔG^o (solv, [Fe$_2$(bdt)CO$_6$]$^{-n}$) (kcal/mol)	ΔG_o (solv, [Fe2(bdt)CO6^{l-n+1}) (kcal/mol)	Redox Potential (eV)
[Fe$_2$(bdt)(CO)$_6$]	[Fe$_2$(bdt)(CO)$_6$]$^{-1}$	-44.2	-78.70	-38.56	-4.06	-1.59
[Fe$_2$(bdt)(CO)$_6$]	[Fe$_2$(bdt)μCO-(CO)$_5$]$^{-1}$	-43.55	-78.66	-39.17	-4.06	-1.59
[Fe$_2$(bdt)(CO)$_6$]$^{-1}$	[Fe$_2$(bdt)μCO-(CO)$_5$]$^{-2}$	19.31	-89.23	-147.10	-38.56	-1.13
[Fe$_2$(bdt)μCO-(CO)$_5$]$^{-1}$	[Fe$_2$(bdt)μCO-(CO)$_5$]$^{-2}$	18.66	-89.27	-147.10	-39.17	-1.13

Table 3. Redox parameters calculated using BP86 as basis set.

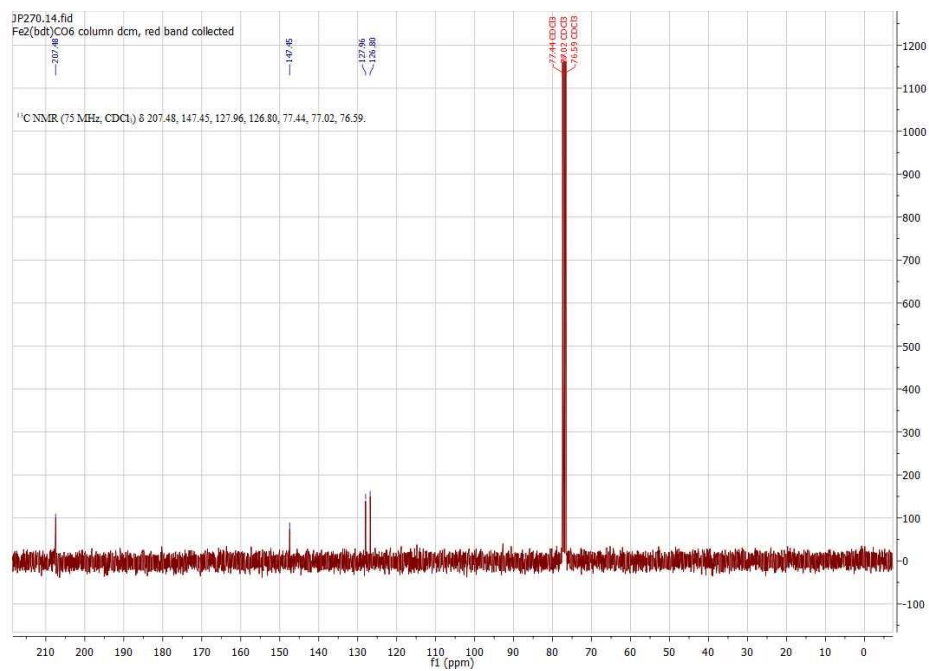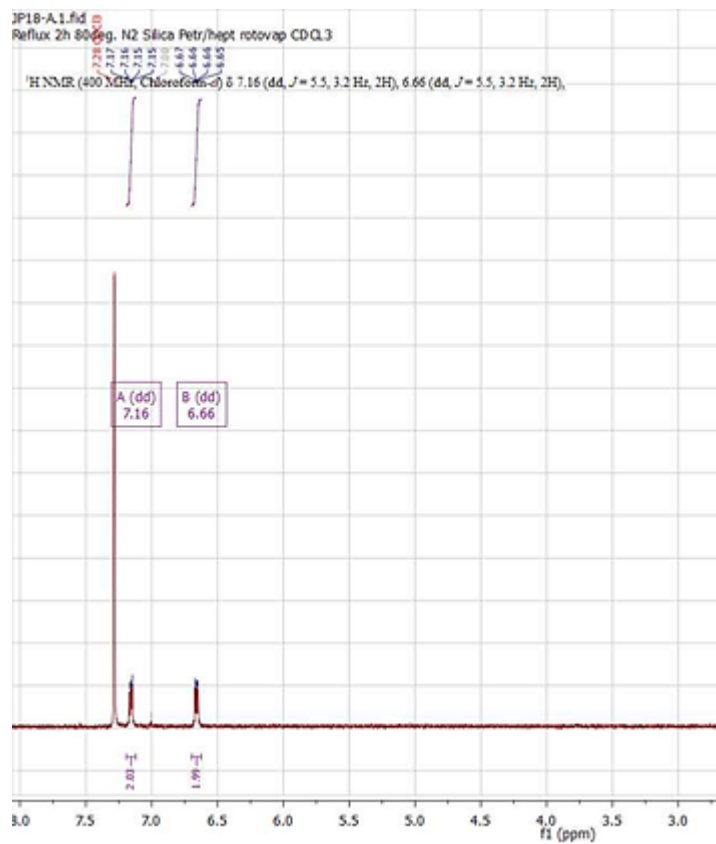| Starting product	Final product	ΔG^o (gas, redox) (kcal/mol)	ΔG^o (solution, redox) (kcal/mol)	ΔG^o (solv, [Fe$_2$(bdt)(CO)$_6$]$^{-n}$) (kcal/mol)	ΔG_o (solv, [Fe2(bdt)(CO)$_6$]$^{l-n+1}$) (kcal/mol)	Redox Potential (eV)
[Fe$_2$(bdt)(CO)$_6$]	[Fe$_2$(bdt)(CO)$_6$]$^{-1}$	-50.47	-84.14	-38.17	-4.50	-1.41
[Fe$_2$(bdt)(CO)$_6$]	[Fe$_2$(bdt)μCO-(CO)$_5$]$^{-1}$	-48.89	-82.01	-37.62	-4.50	-1.50
[Fe$_2$(bdt)(CO)$_6$]$^{-1}$	[Fe$_2$(bdt)μCO-(CO)$_5$]$^{-2}$	15.25	-92.11	-145.53	-38.17	-1.07
[Fe$_2$(bdt)μCO-(CO)$_5$]$^{-1}$	[Fe$_2$(bdt)μCO-(CO)$_5$]$^{-2}$	13.67	-94.24	-145.53	-37.62	-0.97

5. TD-DFT XANES calculations

Below are given the SFO of the most contributing molecular orbitals (MO's) in the TD-DFT XANES calculations. The first tables; 105A, 106A, 114A, 126A, 127A, 130A and 141A represent the neutral $[Fe_2(bdt)(CO)_6]$ molecule. Whereas the tables; 107A, 108A, 118A, 121A, 122A, 130A and 129A represent the contributions of $[Fe_2(bdt)\mu\text{-}CO(CO)_5]^{2-}$. Each percentage contribution in the table below corresponds to the indicated SFO. In general, a SFO may be a linear combination of several Fragment Orbitals on the same, or on symmetry-related Fragments. Only the first 'member' of such a combination is specified here.

105A LUMO				106 A			
18.66%	1 D:x^2-y^2	Fe			15.30%	1 D:z^2	Fe
11.29%	1 D:xy	Fe			12.47%	1 D:xz	Fe
6.83%	1 D:yz	Fe			5.26%	2 P:x	S
6.79%	2 P:x	S			3.52%	1 D:xy	Fe
3.42%	1 D:xz	Fe			3.22%	1 P:x	C
3.35%	1 D:xz	Fe			3.14%	1 P:x	C
3.19%	2 P:z	S			2.85%	1 P:x	C

114 A				126 A			
13.79%	1 P:x	C			12.72%	2 S	H
6.41%	1 P:x	C			10.30%	2 S	H
5.58%	1 P:z	C			3.91%	2 P:y	C
5.51%	1 P:y	C			3.74%	2 P:z	S
5.19%	1 P:x	O			3.73%	2 P:y	S
3.63%	1 P:z	C			2.96%	2 P:y	C
2.69%	1 P:x	C					
2.67%	1 P:z	C					

127 A				130 A		
5.60%	3 S	O		7.05%	3 S	O
4.28%	3 S	O		6.55%	3 S	O
4.20%	3 S	O		6.39%	3 S	O
4.06%	3 S	O		5.56%	3 S	O
3.97%	3 S	O		5.35%	2 P:x	C
3.07%	3 S	O		5.26%	2 P:z	C
				4.99%	2 P:x	C
				4.74%	3 S	O
				4.57%	2 P:z	C
				4.45%	3 S	O
				4.35%	2 P:x	C
				3.86%	2 P:x	C

141A		
7.99%	2 P:x	O
4.63%	2 P:z	O
3.89%	2 P:x	C
3.49%	2 P:y	C

107A LUMO	9.59%	1 D:x^2-y^2	Fe		108 A	8.67%	1 P:x	C
	7.75%	1 D:xy	Fe			8.58%	1 P:x	C
	5.96%	1 P:x	C			7.03%	2 S	H
	4.30%	2 P:x	S			4.00%	1 P:x	C
	3.89%	2 S	H			3.53%	2 S	H
	3.81%	2 S	H			3.52%	1 P:x	C
	3.80%	1 P:x	C			3.09%	1 P:x	C
	3.44%	1 P:x	C			3.05%	1 P:z	C
	3.02%	1 P:y	C					
	3.01%	1 P:y	C					

118 A	10.71%	3 S	O		121A	12.89%	1 D:z^2	Fe
	8.25%	1 P:y	C			11.92%	1 P:z	C
	7.83%	5 S	Fe			8.54%	1 P:y	C
	4.87%	1 D:x^2-y^2	Fe			5.86%	1 P:x	C
	3.59%	3 S	O			5.63%	1 P:x	C
	3.55%	2 P:x	C			3.92%	1 P:z	C
	3.14%	3 S	O			3.02%	1 D:xy	Fe

122 A	27.70%	1 P:z	C		129 A	5.48%	3 S	O
	9.49%	1 P:z	O			4.30%	3 S	O
	6.00%	1 P:z	C			4.30%	1 D:x^2-y^2	Fe
	5.76%	1 D:xz	Fe			3.71%	1 P:y	C
	5.51%	1 P:z	C			3.63%	1 D:x^2-y^2	Fe
						3.61%	2 S	C
						3.20%	1 P:z	C

6. ^1H – and ^{13}C – NMR spectrum of $[Fe_2(bdt)(CO)_6]$

JP18-A.1.fid
Reflux 2h 80 deg. N2 Silica Petr/hept rotovap CDCl3

^1H NMR (400 MHz, Chloroform-d) δ 7.16 (dd, J = 5.5, 3.2 Hz, 2H), 6.66 (dd, J = 5.5, 3.2 Hz, 2H).

A (dd) 7.16
B (dd) 6.66

JP270.14.fid
Fe2(bdt)CO6 column dcm, red band collected

^{13}C NMR (75 MHz, CDCl3) δ 207.48, 147.45, 127.96, 126.80, 77.44, 77.02, 76.59.

7.References

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