Supporting Information for: CASPT2 molecular geometries of Fe(II) spin-crossover complexes

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Table S1: CASPT2/cc-pVTZ computed Fe-L bond distances (in Angstrom) for $[FeL_6]^{2+}$ where, L = NH_3, NCH, PH_3, CO and CNH. DFT/def2-TZVP bond distances are also included for comparison.

		Fe-L Distances	
L	**Method**	**HS**	**LS**
NH_3	CASPT2	2.257, 2.258, 2.258	1.990, 1.996, 2.091
		2.258, 2.262, 2.264	2.091, 2.091, 2.092
	TPSSh	2.273, 2.275, 2.276	2.079, 2.080, 2.080
		2.280, 2.294, 2.294	2.080, 2.080, 2.080
	PBE	2.279, 2.280, 2.283	2.073, 2.073, 2.073
		2.286, 2.300, 2.300	2.073, 2.074, 2.074
	M06	2.251, 2.253, 2.270	2.086, 2.087, 2.088
		2.271, 2.283, 2.285	2.088, 2.093, 2.094
	M06-L	2.240, 2.241, 2.262	2.081, 2.081, 2.081
		2.262, 2.273, 2.274	2.083, 2.086, 2.086
NCH	CASPT2	2.154, 2.154, 2.163	1.907, 1.907, 1.907
		2.164, 2.164, 2.165	1.907, 1.907, 1.907
	TPSSh	2.159, 2.159, 2.161	1.928, 1.928, 1.928
		2.161, 2.170, 2.170	1.928, 1.928, 1.928
	PBE	2.150, 2.150, 2.150	1.908, 1.908, 1.908
		2.150, 2.176, 2.176	1.908, 1.908, 1.908
	M06	2.162, 2.162, 2.166	1.943, 1.943, 1.943
		2.166, 2.167, 2.167	1.943, 1.943, 1.943
	M06-L	2.190, 2.190, 2.190	1.959, 1.959, 1.960
		2.190, 2.192, 2.192	1.960, 1.960, 1.960
PH_3	CASPT2	2.596, 2.596, 2.617	2.207, 2.207, 2.209
		2.617, 2.618, 2.618	2.209, 2.211, 2.211
	TPSSh	2.624, 2.625, 2.632	2.262, 2.262, 2.262
		2.633, 2.662, 2.664	2.262, 2.262, 2.263
	PBE	2.571, 2.571, 2.591	2.247, 2.247, 2.248
		2.593, 2.628, 2.630	2.248, 2.248, 2.249
	M06	2.609, 2.634, 2.635	2.272, 2.273, 2.273
		2.635, 2.648, 2.657	2.274, 2.275, 2.275
	M06-L	2.573, 2.575, 2.597	2.249, 2.249, 2.250
		2.602, 2.604, 2.609	2.250, 2.250, 2.253
CO	CASPT2	2.283, 2.284, 2.286	1.863, 1.863, 1.864
		2.286, 2.323, 2.325	1.864, 1.864, 1.864
	TPSSH	2.263, 2.263, 2.264	1.919, 1.919, 1.919
		2.264, 2.330, 2.331	1.919, 1.919, 1.919
	PBE	2.219, 2.219, 2.221	1.894, 1.894, 1.894
		2.221, 2.319, 2.319	1.894, 1.894, 1.894
	M06	2.288, 2.288, 2.288	1.933, 1.933, 1.933
		2.288, 2.344, 2.345	1.933, 1.933, 1.933
	M06-L	2.299, 2.300, 2.302	1.940, 1.940, 1.940
		2.302, 2.358, 2.358	1.940, 1.940, 1.940
CNH	CASPT2	2.203, 2.203, 2.203	1.845, 1.845, 1.846
		2.203, 2.255, 2.255	1.846, 1.864, 1.846
	TPSSh	2.212, 2.213, 2.213	1.901, 1.901, 1.901
		2.213, 2.268, 2.268	1.901, 1.901, 1.901
	PBE	2.178, 2.179, 2.179	1.882, 1.882, 1.882
		2.179, 2.259, 2.260	1.882, 1.882, 1.882
	M06	2.241, 2.242, 2.247	1.917, 1.917, 1.919
		2.247, 2.301, 2.302	1.919, 1.919, 1.919
	M06-L	2.174, 2.175, 2.196	1.885, 1.885, 1.887
		2.198, 2.205, 2.207	1.887, 1.887, 1.887

Table S2: CASPT2 computed Fe-L bond distances (in Angstrom) for $[FeL_6]^{2+}$ where, L = NCH and CO as a function of active space and basis set. The atoms with the cc-pVTZ basis set are noted; all remaining atoms are treated with cc-pVDZ basis set.

L	Active Space	Basis set	Fe-L Distances	
			HS	LS
NCH	6*e*,5*o*	all	2.169, 2.169, 2.174	1.953, 1.953, 1.953
			2.174, 2.176, 2.176	1.953, 1.953, 1.953
	6*e*,5*o*	Fe	2.172, 2.172, 2.174	1.955, 1.955, 1.955
			2.174, 2.177, 2.177	1.955, 1.955, 1.955
	6*e*,5*o*	Fe, N	2.169, 2.169, 2.169	1.951, 1.951, 1.951
			2.169, 2.174, 2.174	1.951, 1.951, 1.951
	6*e*,5*o*	None	2.189, 2.189, 2.190	1.977, 1.977, 1.977
			2.190, 2.192, 2.192	1.977, 1.977, 1.977
	6*e*,10*o*	Fe	2.177, 2.177, 2.177	1.961, 1.961, 1.962
			2.177, 2.178, 2.178	1.962, 1.962, 1.962
	10*e*,12*o*	all	2.154, 2.154, 2.163	1.907, 1.907, 1.907
			2.164, 2.164, 2.165	1.907, 1.907, 1.907
	10*e*,12*o*	Fe	2.152, 2.142, 2.176	1.927, 1.938, 1.952
			2.185, 2.186, 2.186	1.953, 1.969, 1.974
CO	6*e*,5*o*	all	2.281, 2.281, 2.290	1.798, 1.798, 1.798
			2.290, 2.319, 2.319	1.798, 1.798, 1.798
	6*e*,5*o*	Fe	2.281, 2.281, 2.290	1.819, 1.819, 1.819
			2.290, 2.316, 2.316	1.819, 1.819, 1.819
	6*e*,5*o*	None	2.294, 2.294, 2.303	1.842, 1.842, 1.842
			2.303, 2.329, 2.329	1.842, 1.842, 1.842
	6*e*,10*o*	Fe	2.290, 2.290, 2.298	1.871, 1.871, 1.871
			2.298, 2.324, 2.324	1.871, 1.871, 1.871
	10*e*,12*o*	all	2.299, 2.300, 2.302	1.940, 1.940, 1.940
			2.302, 2.358, 2.358	1.940, 1.940, 1.940
	10*e*,12*o*	Fe	2.285, 2.285, 2.289	1.894, 1.894, 1.894
			2.289, 2.318, 2.318	1.894, 1.894, 1.894

Table S3: Fe-N bond distances (in Angstrom) of the $[Fe(tacn)_2]^{2+}$ complex as a function of basis set and active space. The atoms with the cc-pVTZ basis set are noted; all remaining atoms are treated with cc-pVDZ basis set.

Active Space	Basis Set	Fe-N Distances	
		HS	LS
6*e*,5*o*	all	2.209, 2.209, 2.222	2.034, 2.034, 2.034
		2.222, 2.224, 2.225	2.034, 2.034, 2.034
	Fe, N	2.207, 2.207, 2.221	2.034, 2.034, 2.035
		2.221, 2.223, 2.223	2.035, 2.035, 2.035
	Fe	2.215, 2.215, 2.223	2.035, 2.035, 2.036
		2.222, 2.223, 2.224	2.036, 2.037, 2.037
	none	2.215, 2.216, 2.222	2.043, 2.043, 2.043
		2.223, 2.223, 2.223	2.043, 2.044, 2.044
6*e*,10*o*	Fe	2.212, 2.214, 2.224	2.036, 2.036, 2.038
		2.225, 2.228, 2.229	2.038, 2.038, 2.038
10*e*,12*o*	Fe	2.212, 2.212, 2.225	2.026, 2.029, 2.034
		2.226, 2.226, 2.227	2.038, 2.042, 2.042

Table S4: DFT/def2-TZVP optimized Fe-N bond distances (in Angstrom) for the $[Fe(tacn)_2]^{2+}$ complex.

Functional	Fe-N Distance	
	HS	LS
TPSSH	2.243, 2.244, 2.251	2.048, 2.049, 2.049
	2.253, 2.253, 2.253	2.049, 2.049, 2.050
PBE	2.253, 2.254, 2.259	2.044, 2.044, 2.044
	2.260, 2.262, 2.262	2.045, 2.045, 2.045
M06	2.215, 2.219, 2.234	2.055, 2.058, 2.060
	2.245, 2.249, 2.254	2.061, 2.067, 2.067
M06-L	2.239, 2.242, 2.258	2.060, 2.062, 2.066
	2.262, 2.263, 2.264	2.067, 2.067, 2.070

Table S5: CASPT2 and DFT computed Fe-N bond distances (in Angstrom) for the $[Fe(bpy)_3]^{2+}$ complex. For the CASPT2 calculations cc-pVTZ basis set is used for the Fe and cc-pVDZ for the rest of the elements. DFT optimizations are performed with def2-TZVP basis set.

Functional	Fe-N Distance	
	HS	LS
CASPT2	2.167, 2.168, 2.168	1.938, 1.939, 1.940
	2.168, 2.181, 2.182	1.940, 1.946, 1.946
TPSSh	2.181, 2.183, 2.187	1.983, 1.983, 1.984
	2.189, 2.204, 2.204	1.984, 1.985, 1.986
PBE	2.168, 2.174, 2.177	1.971, 1.971, 1.971
	2.189, 2.191, 2.199	1.972, 1.972, 1.973
M06	2.188, 2.188, 2.189	1.989, 1.991, 2.003
	2.195, 2.200, 2.205	2.008, 2.009, 2.014
M06-L	2.148, 2.159, 2.183	1.968, 1.971, 1.983
	2.185, 2.186, 2.197	1.996, 1.999, 2.001

Table S6: CASPT2 and DFT computed Fe-N bond distances (in Angstrom) for the $[Fe(pic)_3]^{2+}$ complex. For the CASPT2 calculations cc-pVTZ basis set is used for the Fe and cc-pVDZ for the rest of the elements. DFT optimizations are performed with def2-TZVP basis set.

	Fe-N Distance			
	HS		LS	
Functional	**Fe-$N_{pyridine}$**	**Fe-N_{amine}**	**Fe-$N_{pyridine}$**	**Fe-N_{amine}**
CASPT2	2.186, 2.186 2.189	2.232, 2.235 2.236	1.954, 1.958, 1.980	2.021, 2.032 2.035
TPSSh	2.192, 2.205 2.210	2.267, 2.270 2.271	1.991, 1.995 1.997	2.051, 2.051 2.053
PBE	2.189, 2.195 2.205	2.276, 2.277 2.285	1.967, 1.970 1.971	2.049, 2.053 2.054
M06	2.159, 2.188 2.201	2.243, 2.272 2.284	2.005, 2.009 2.024	2.065, 2.072 2.079
M06-L	2.170, 2.177 2.196	2.243, 2.267 2.278	1.984, 1.987 2.005	2.058, 2.073 2.077

Table S7. Percent contributions from the HF determinant to the CASSCF wavefunction. Results are reported on the CASPT2 minimum geometry and the cc-pVTZ basis set was used on all atoms.

Complex	HS contribution	LS contribution
$[Fe(NH_3)_6]^{2+}$	0.974	0.964
$[Fe(NCH)_6]^{2+}$	0.934	0.934
$[Fe(PH_3)_6]^{2+}$	0.832	0.878
$[Fe(CO)_6]^{2+}$	0.975	0.896
$[Fe(CNH)_6]^{2+}$	0.978	0.946

Table S8. Coupled cluster T1 amplitudes from the calculation with frozen 3s3p orbitals. Values greater than 0.02 are indicative of multireference character.

Complex	HS contribution	LS contribution
$[Fe(NH_3)_6]^{2+}$	0.01414	0.02187
$[Fe(NCH)_6]^{2+}$	0.01656	0.02670
$[Fe(PH_3)_6]^{2+}$	0.02148	0.05037
$[Fe(CO)_6]^{2+}$	0.02106	0.03841
$[Fe(CNH)_6]^{2+}$	0.01941	0.03853

Table S9. CASPT2 vibrational frequencies in cm^{-1} for HS state of the $[Fe(tacn)_2]^{2+}$ complex computed with the minimal (6*e*,5*o*) active space and the cc-pVDZ basis set on all atoms.

Frequencies					
0.00	0.00	0.00	0.00	0.00	0.00
39.24	41.63	70.06	117.92	136.44	151.48
168.11	186.63	189.27	192.24	197.22	234.53
263.07	278.06	301.37	310.18	313.64	315.30
317.46	393.32	394.31	397.69	401.14	405.93
408.76	461.19	473.83	553.15	553.52	565.95
566.37	592.24	595.74	782.03	785.01	793.20
796.39	833.43	835.80	870.40	879.02	879.17
880.47	881.39	883.80	941.05	956.83	990.50
996.18	998.61	999.05	1039.32	1045.55	1047.71
1053.19	1059.71	1060.22	1099.35	1100.65	1116.96
1119.01	1135.37	1135.68	1137.85	1138.98	1175.74
1177.05	1177.74	1179.08	1259.59	1260.84	1264.14
1264.44	1291.35	1292.86	1293.41	1295.25	1311.13
1311.20	1320.33	1323.62	1369.15	1369.98	1371.92
1394.24	1395.55	1396.13	1396.70	1399.87	1406.07
1406.20	1406.82	1409.48	1453.87	1457.57	1462.65
1463.51	1464.80	1466.36	1482.04	1484.67	1487.40
1487.72	1494.95	1496.91	1497.03	1497.19	1498.21
1499.52	1515.13	1515.59	3087.99	3088.13	3088.92
3089.33	3090.48	3090.98	3119.13	3120.27	3121.60
3122.16	3126.83	3127.30	3148.90	3149.77	3150.14
3150.71	3151.42	3152.04	3180.28	3181.15	3183.26
3183.70	3192.79	3193.05	3523.29	3524.39	3524.72
3524.81	3525.45	3525.86			

Table S10. CASPT2 vibrational frequencies in cm^{-1} for LS state of the $[Fe(tacn)_2]^{2+}$ complex computed with the minimal (6*e*,5*o*) active space and the cc-pVDZ basis set on all atoms.

Frequencies LS					
0.00	0.00	0.00	0.00	0.00	0.00
94.37	123.40	123.41	184.59	184.75	191.12
209.15	209.34	223.19	223.21	318.05	322.16
330.89	330.95	346.13	366.19	366.31	387.56
387.76	410.50	428.68	428.71	449.97	455.80
455.91	505.56	508.25	573.94	574.11	609.71
609.82	615.29	623.69	802.59	802.74	823.50
823.68	850.36	855.21	883.20	887.81	900.21
900.30	902.63	902.69	982.29	993.84	1001.13
1001.22	1003.90	1004.00	1064.41	1065.15	1065.16
1066.07	1075.67	1075.75	1099.16	1104.79	1110.00
1116.63	1140.11	1140.30	1147.27	1147.39	1170.03
1170.14	1173.06	1173.18	1255.38	1255.43	1259.43
1259.47	1291.52	1291.56	1296.98	1297.03	1304.09
1304.78	1317.10	1324.29	1368.61	1369.28	1393.05
1393.16	1393.68	1396.09	1396.21	1401.85	1404.13
1404.22	1412.23	1412.33	1454.83	1461.52	1461.58
1461.72	1466.84	1466.98	1486.09	1486.19	1490.50
1490.63	1501.86	1501.88	1502.38	1503.47	1508.57
1508.63	1516.63	1517.04	3098.63	3099.12	3099.31
3099.89	3099.91	3100.55	3123.99	3124.55	3124.79
3124.90	3129.46	3129.74	3159.86	3160.50	3160.82
3161.31	3161.38	3161.93	3185.82	3186.24	3186.49
3186.63	3196.01	3196.22	3517.22	3517.50	3517.61
3517.97	3518.13	3518.34			