Supporting information

for

Theoretical evidence for the direct ^{3}MLCT–HS deactivation in the light-induced spin crossover of Fe(II)-polypyridyl complexes

by

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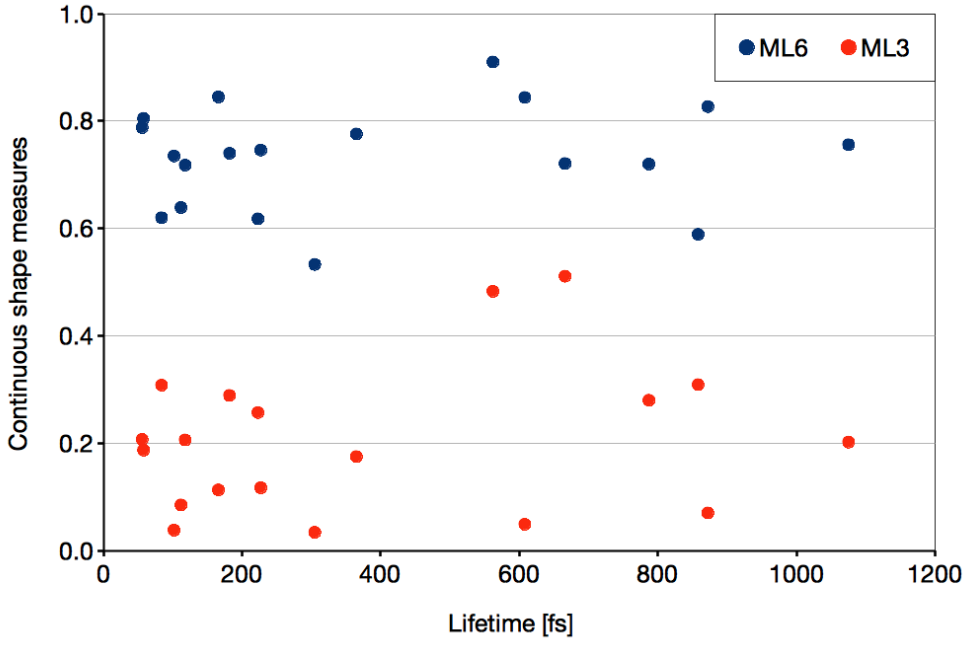
S1. Continuous shape measures versus spin orbit coupling and ^{3}MLCT lifetimes

Conformation	ML6 [a]	ML3 [b]	Average SO [cm^{-1}]	Lifetime [fs]
1	0.827	0.070	14	872
2	0.533	0.034	21	305
3	0.967	0.004	7	2889
4	0.639	0.085	33	112
5	0.844	0.049	14	608
6	0.788	0.207	46	56
7	0.618	0.257	28	223
8	0.620	0.308	43	84
9	0.589	0.309	13	858
10	0.721	0.511	13	666
11	0.845	0.113	30	166
12	0.718	0.206	32	118
13	0.740	0.289	27	182
14	0.805	0.187	48	58
15	0.910	0.483	16	562
16	0.720	0.280	13	787
17	0.776	0.175	20	365
18	0.735	0.038	40	102
19	0.756	0.202	13	1075
20	0.746	0.117	20	227

[a] Deviation of the Fe(II)N_6 cage from the perfect octahedron.
[b] Deviation of the triangle formed by the three C-C bond midpoints of each bipyridine ligand from an equilateral triangle

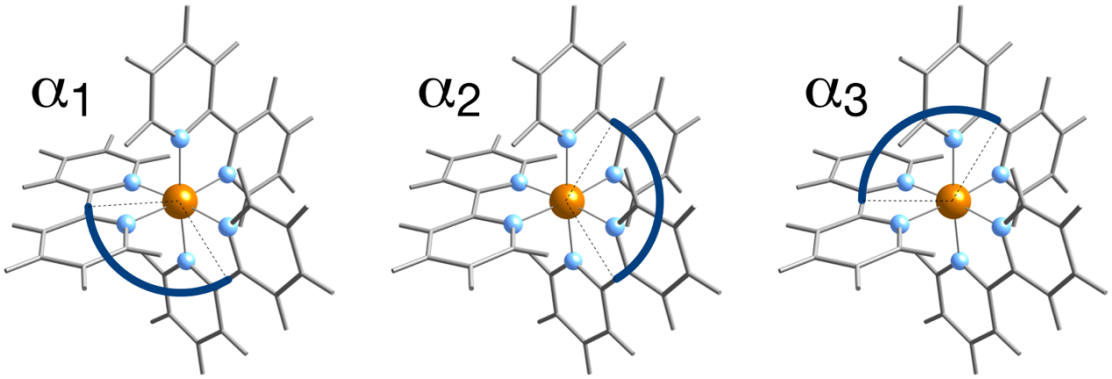


Conformation 3 with a lifetime of 2889 fs is not included to improve the clarity of the graph.

S2-a. Angles between the bipyridine ligands (α) versus ^{3}MLCT lifetimes

Conformation	α_1	α_2	α_3	Avg. dev. [a]	Max. dev. [b]	Lifetime [fs]
1	125.1	118.8	116.0	3.4	5.1	872
2	120.3	117.2	122.4	1.9	2.9	305
3	119.8	120.4	119.8	0.3	0.4	2889
4	119.9	117.1	122.9	2.0	2.9	112
5	120.7	119.8	119.1	0.6	0.9	608
6	126.7	116.4	116.5	4.6	6.7	56
7	115.8	128.6	115.2	5.9	8.6	223
8	129.0	118.5	112.2	6.1	9.0	84
9	110.3	125.5	124.0	6.4	9.7	858
10	127.2	123.8	108.6	7.5	11.4	666
11	121.7	124.1	114.2	3.9	5.8	166
12	126.3	112.9	120.8	4.8	7.1	118
13	119.5	111.9	128.6	5.7	8.6	182
14	127.4	120.0	112.7	4.9	7.4	58
15	111.1	118.6	130.2	6.8	10.2	562
16	127.6	111.5	120.6	5.5	8.5	787
17	124.1	113.1	124.1	5.0	6.9	365
18	122.8	118.6	118.4	1.9	2.8	102
19	127.1	116.9	115.8	4.8	7.1	1075
20	114.4	121.7	123.8	3.7	5.6	227

[a,b] Average and maximum deviation from the 120º of the D_3 structure



S2-b. Shortest, longest and average Fe-N distances (in Å) versus ^{3}MLCT lifetimes

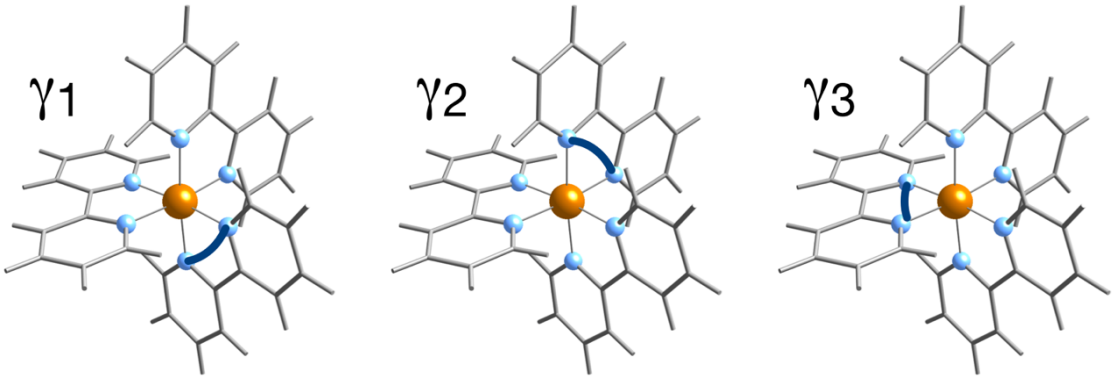
Conformation	shortest	longest	average	Avg. dev. [a]	Max. dev. [b]	Lifetime [fs]
1	1.953	2.048	1.993	0.028	0.071	872
2	1.911	1.999	1.956	0.034	0.066	305
3	1.927	2.012	1.972	0.022	0.050	2889
4	1.956	2.055	2.010	0.040	0.078	112
5	1.898	1.989	1.966	0.020	0.079	608
6	1.901	1.974	1.934	0.043	0.076	56
7	1.951	2.024	1.982	0.020	0.047	223
8	1.956	2.038	2.006	0.036	0.061	84
9	1.944	1.977	1.957	0.020	0.033	858
10	1.947	2.005	1.970	0.018	0.030	666
11	1.958	2.101	2.004	0.038	0.124	166
12	1.947	2.018	1.981	0.032	0.041	118
13	1.925	2.042	1.967	0.032	0.065	182
14	1.968	2.033	1.996	0.024	0.056	58
15	1.971	2.010	1.986	0.013	0.033	562
16	1.927	1.996	1.963	0.022	0.050	787
17	1.897	2.054	1.991	0.061	0.080	365
18	1.909	2.053	1.994	0.039	0.076	102
19	1.905	1.981	1.952	0.027	0.072	1075
20	1.958	1.996	1.980	0.014	0.019	227

[a,b] Average and maximum deviation from the average Fe-N distance (1.978 Å)

S2-c. Bite angles γ (in degrees) of the bipyridine ligands versus ^{3}MLCT lifetimes

Conformation	γ_1	γ_2	γ_3	Avg. dev. [a]	Max. dev. [b]	Lifetime [fs]
1	80.5	82.7	79.9	1.3	1.5	872
2	83.8	82.0	81.1	1.1	2.4	305
3	80.7	78.5	79.7	1.8	2.9	2889
4	84.4	81.7	78.9	1.9	3.0	112
5	82.9	83.8	80.1	1.8	2.4	608
6	81.7	82.2	79.3	1.1	2.1	56
7	81.6	83.0	81.1	0.7	1.6	223
8	83.3	81.1	81.2	0.8	1.9	84
9	83.0	79.7	81.3	1.1	1.7	858
10	81.6	79.9	81.9	0.7	1.5	666
11	81.0	82.8	80.5	0.9	1.4	166
12	81.2	81.3	81.1	0.2	0.3	118
13	82.1	78.8	82.0	1.3	2.6	182
14	81.1	79.5	82.9	1.2	1.9	58
15	82.6	79.4	80.9	1.2	2.0	562
16	81.7	78.8	82.2	1.2	2.6	787
17	80.7	78.9	82.8	1.5	2.5	365
18	82.6	81.9	82.0	0.8	1.2	102
19	82.4	80.9	79.9	1.0	1.5	1075
20	81.5	80.9	81.0	0.4	0.5	227

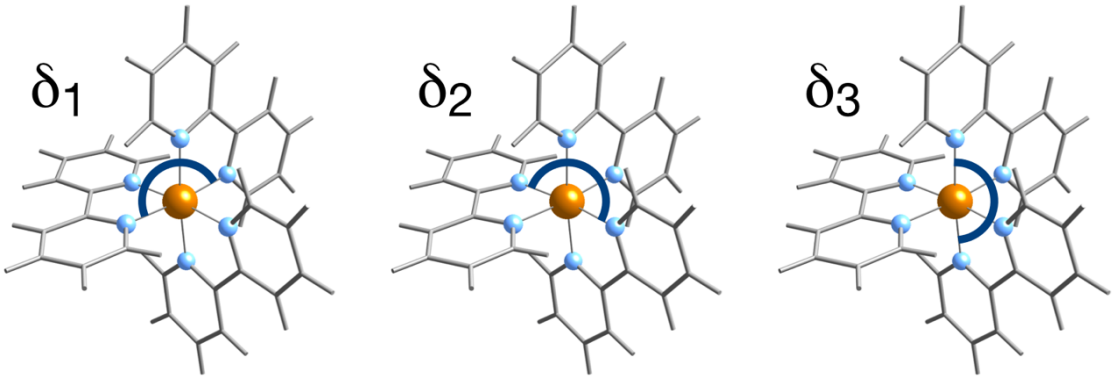
[a,b] Average and maximum deviation from the average bite angle (81.3º)



S2-d. N-Fe-N (nearly) linear angles δ (in degrees) versus ^{3}MLCT lifetimes

Conformation	δ_1	δ_2	δ_3	Avg. dev. [a]	Max. dev. [b]	Lifetime [fs]
1	173.7	172.6	174.6	0.8	1.4	872
2	174.4	174.5	176.5	1.9	3.3	305
3	172.0	178.7	169.6	3.4	5.5	2889
4	174.4	175.0	174.6	1.5	1.8	112
5	173.8	174.5	174.8	1.2	1.6	608
6	170.7	174.4	176.2	2.2	3.0	56
7	174.0	172.1	170.3	1.6	2.9	223
8	171.2	175.2	169.9	2.4	3.3	84
9	175.1	173.8	173.1	0.9	1.9	858
10	173.3	170.6	174.7	1.4	2.6	666
11	167.6	172.7	171.6	2.6	5.6	166
12	168.3	180.0	172.1	4.3	6.8	118
13	169.3	175.9	178.2	3.8	5.0	182
14	172.3	172.4	172.3	0.9	0.9	58
15	169.7	167.4	172.9	3.2	5.8	562
16	169.4	176.5	169.1	3.7	4.1	787
17	171.2	177.1	170.3	2.9	3.9	365
18	174.4	174.1	175.3	1.4	2.1	102
19	168.7	176.0	170.3	3.4	4.5	1075
20	174.2	167.3	174.0	2.6	5.9	227

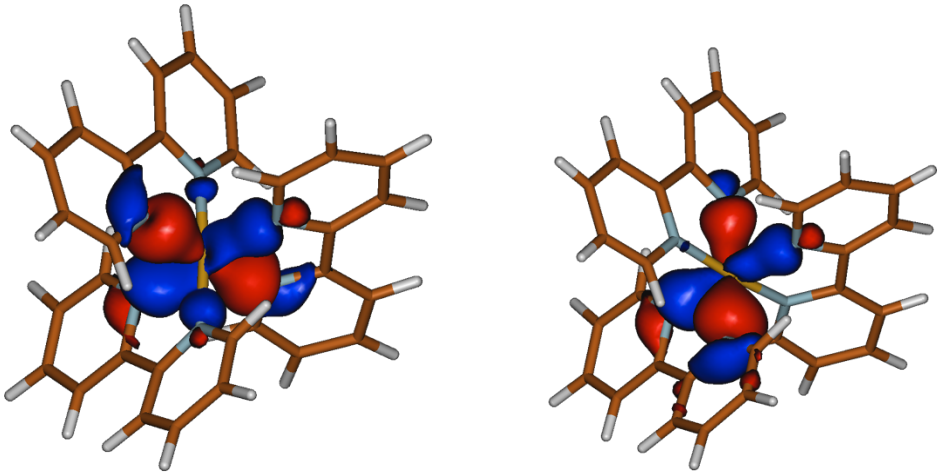
[a,b] Average and maximum deviation from the average N-Fe-N (nearly) linear angle (173.0º)



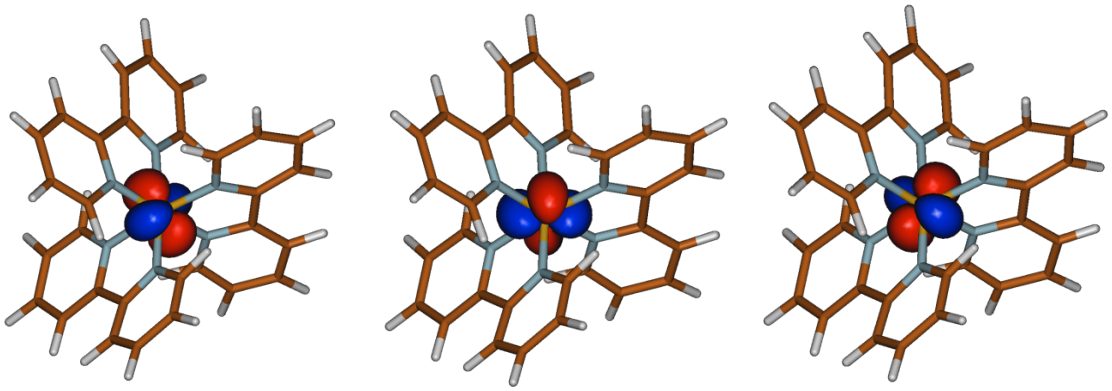
S3. Graphical representation of the active orbitals

Active orbitals of conformation 1, the orbitals of the other conformations are all similar.

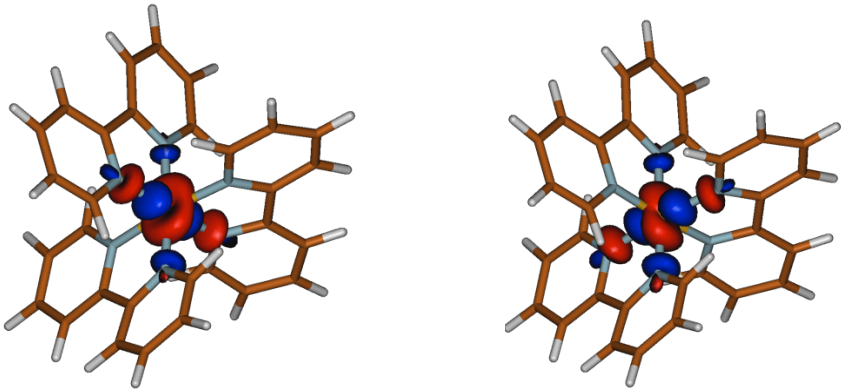
N(σ) orbitals:



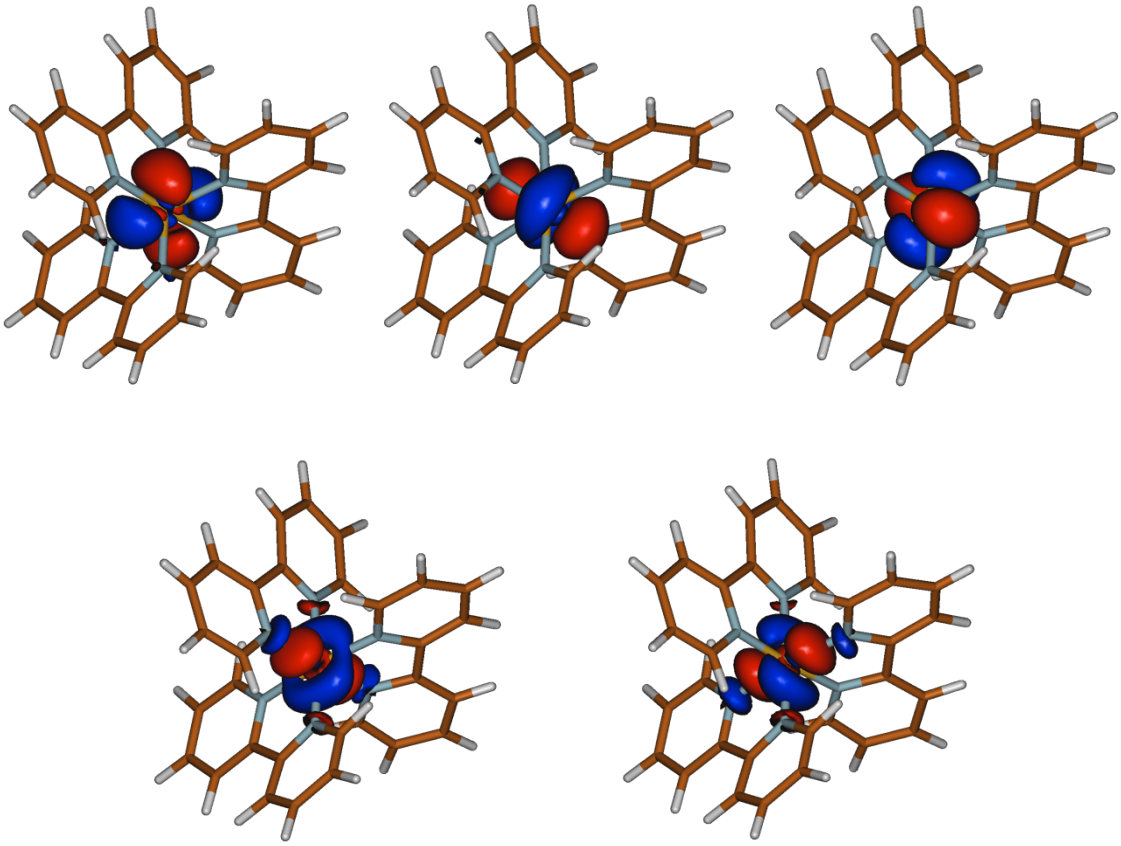
Fe-3d (t_{2g}-like) orbitals:



Fe-3d (e_g-like) orbitals:



Fe-3d’ double-shell orbitals:



Bipyridine π* orbital: