Supporting Information

Probing the photophysical capability of mono and bis(cyclometallated) Fe(II) polypyridine complexes using inexpensive ground state DFT.

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1. Computational methods

Density Functional Theory (DFT) and time-dependent DFT (TDDFT) calculations were performed using Orca 2.8.[1] Geometries were optimized with the PBE0 functional,[2] using the def2-TZVP(-f) basis set for all atoms.[3] Scalar relativity was included using ZORA and Grimme's empirical dispersion correction VDW [4] was used. The revPBE GGA functional was used for the Natural Bond Orbital analysis (NBO 6.0)[5] available in the Orca 3.0.1 package.

Absolute energies were computed through B3LYP* [6] single-point calculations at the PBE0 geometries, which also produced the orbitals shown herein. For the e_g*-like orbitals, the Kohn-Sham orbitals are replaced by the corresponding Pipek-Mezey localized orbitals. The first 100 virtual orbitals were used in the localization procedure performed with the orca_loc program.

The functional used to model the absorption spectra was selected from seven functionals, on the basis of its ability to reproduce the energy and shape of the experimental absorption of complex **1**. TDDFT was then performed on all complexes using the same conditions as before (def2-TZVP(-f) basis set, ZORA scalar relativity, VDW dispersion) using the TPSS non-hybrid functional.[7] An asymptotic correction was applied and solvent effects were included as a continuum using the COSMO model for dichloromethane. 80 roots were computed but only roots with significant oscillator strength are reported in the Tables. In the orca_asa spectral analysis module, a Σ value of 750 cm^{-1} was used as broadening factor of the gaussians (corresponding to FWMH=1766.12 cm^{-1}).

Inclusion of the vibrations in the absorption spectra was achieved using the Orca 3.0.1 program with the B3LYP* functional (this type of calculation requires computing the gradient in the excited state, which is not currently implemented for GGA functionals such as TPSS). Scalar relativity with ZORA and the D2 dispersion keyword (corresponding to VDW in Orca 2.8) were used. The independent mode, displaced harmonic oscillator (IMDHO) model was applied. The same broadening factor was used as for the classical (vibration-free) absorption spectra.

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[1] F. Neese, *WIREs Comput. Mol. Sci.* **2012**, 2, 73.
[2] C. Adamo and V. Barone, *J. Chem. Phys.* **1999**, *110*, 6158.
[3] D. A. Pantazis, X. Y. Chen, C. R. Landis and F. Neese, *J. Chem. Theory Comput.* **2008**, 4, 908.
[4] S. Grimme, *J. Comput. Chem.* **2006**, *27*, 1787.
[5] E. D. Glendening, J. K. Badenhoop, A. E. Reed, J. E. Carpenter, J. A. Bohmann, C. M. Morales, C. R. Landis and F. Weinhold. http://nbo6.chem.wisc.edu.
[6] M. Reiher, O. Salomon, B. A. Hess, *Theor. Chem. Acc.* **2001**, *107*, 48, ; M. Reiher, *Inorg. Chem.* **2002**, *41*, 6928.
[7] V. N. Staroverov, G. E. Scuseria, J. Tao, J. P. Perdew, *J. Chem. Phys.* **2003**, *119*, 12129.

2. Choice of functional for the TDDFT modelling of the absorption spectrum of 1.

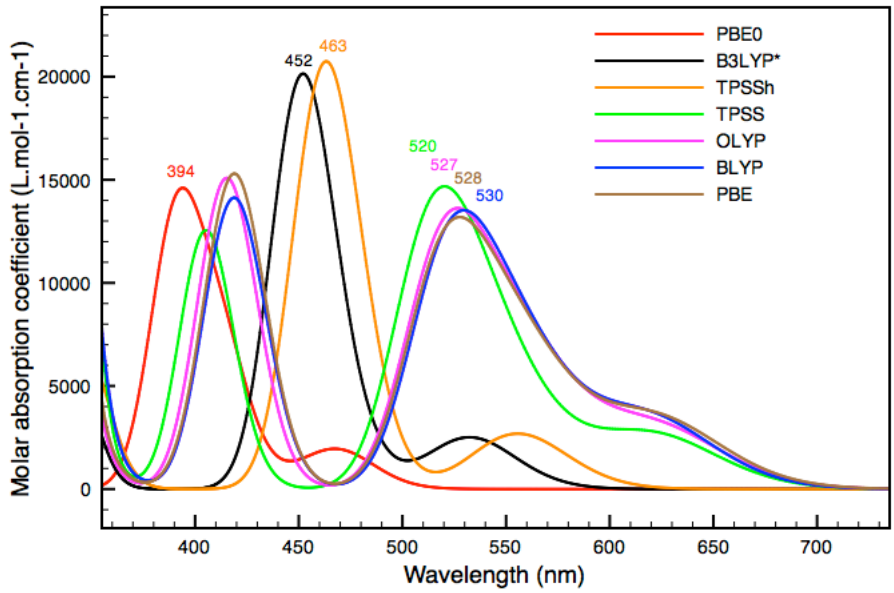


Figure S1 : TDDFT absorption spectrum computed with the seven tested functionals in the 355-755 nm range

Table S1 : Wavelength (nm) and energy (eV) of the second lowest-energy absorption band with the seven tested functionals

	PBE0	B3LYP*	TPSSh	TPSS	OLYP	PBE	BLYP
λ (nm)	394	452	463	520	527	528	530
E (eV)	3.147	2.743	2.678	2.384	2.353	2.348	2.339

3. Effect of the vibrations at 293 K on the TDDFT spectra (zoom on the two lowest energy absorption bands).

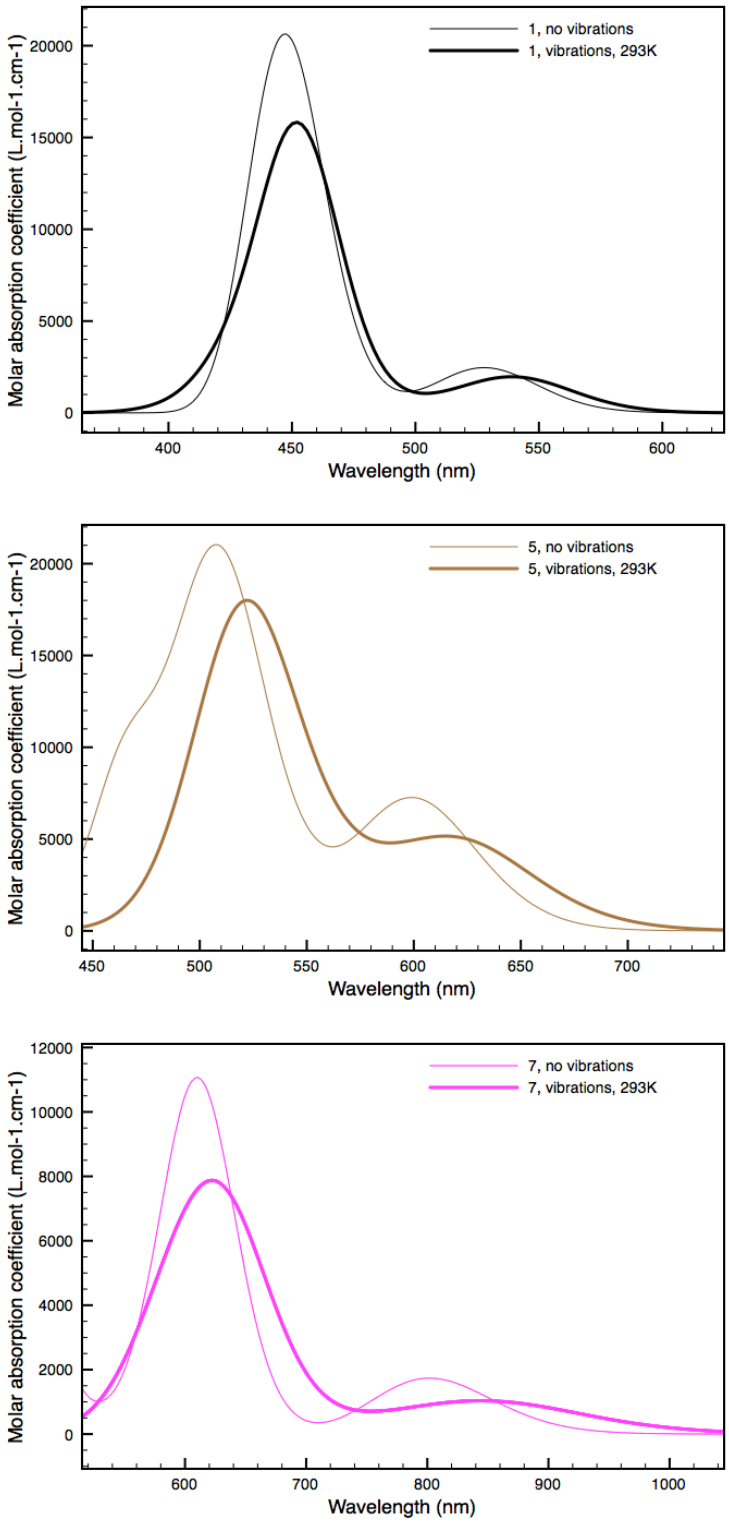


Figure S2 : Including vibrations (thick lines) in the calculation of the TDDFT absorption spectra (thin lines) of complexes **1** (top), **5** (centre) and **7** (bottom).

4a. Data on $Fe(tpy)_2^{2+}$ (1) (E=-2762.067979397 a.u.)

Cartesian coordinates

Fe	5.442593	8.549498	4.751188
N	4.644907	6.747158	4.780254
N	5.245669	8.350327	6.611916
N	6.174570	10.288821	5.321228
N	3.692469	9.361225	4.346986
N	5.641593	8.754043	2.892160
N	7.252601	7.795652	4.555146
C	4.363779	5.977827	3.731250
H	4.607866	6.392122	2.760760
C	3.793821	4.722251	3.858264
H	3.583669	4.134678	2.974259
C	3.503552	4.245229	5.126754
H	3.058030	3.267373	5.260896
C	3.792169	5.040278	6.224351
H	3.579284	4.700046	7.229201
C	4.361858	6.285023	6.020303
C	4.713485	7.220272	7.090588
C	4.548453	7.043918	8.456089
H	4.115502	6.133201	8.848249
C	4.949011	8.065965	9.306739
H	4.828050	7.954716	10.377341
C	5.502782	9.230685	8.791045
H	5.817467	10.032058	9.446102
C	5.639923	9.343650	7.415798
C	6.186830	10.472948	6.661937
C	6.677376	11.632633	7.236506
H	6.675928	11.747137	8.313095
C	7.166341	12.635529	6.414855
H	7.555730	13.552056	6.840739
C	7.147958	12.445111	5.042310
H	7.517757	13.202958	4.363936
C	6.643970	11.257269	4.538819
H	6.611333	11.064135	3.473948
C	2.717942	9.639713	5.209302
H	2.916198	9.391352	6.244487
C	1.518338	10.212420	4.820372
H	0.757341	10.422173	5.560628
C	1.321002	10.506733	3.480694
H	0.394864	10.956154	3.143897
C	2.330032	10.218287	2.575996
H	2.211081	10.435769	1.522511
C	3.503052	9.647053	3.037984
C	4.642042	9.296414	2.188576
C	4.759576	9.468225	0.817622

H	3.952786	9.903878	0.243514
C	5.937076	9.067558	0.199917
H	6.054732	9.192340	-0.869659
C	6.964637	8.507071	0.947325
H	7.885967	8.192100	0.476155
C	6.782044	8.360820	2.314220
C	7.720089	7.795214	3.285363
C	8.969202	7.291649	2.966071
H	9.312301	7.304914	1.939967
C	9.762854	6.772111	3.976229
H	10.743096	6.370616	3.750895
C	9.280462	6.773856	5.275392
H	9.866353	6.377327	6.094103
C	8.021265	7.295506	5.519421
H	7.603162	7.316964	6.518482

Figure S4 : Computed UV-Vis absorption spectrum in the 235-725 nm range.

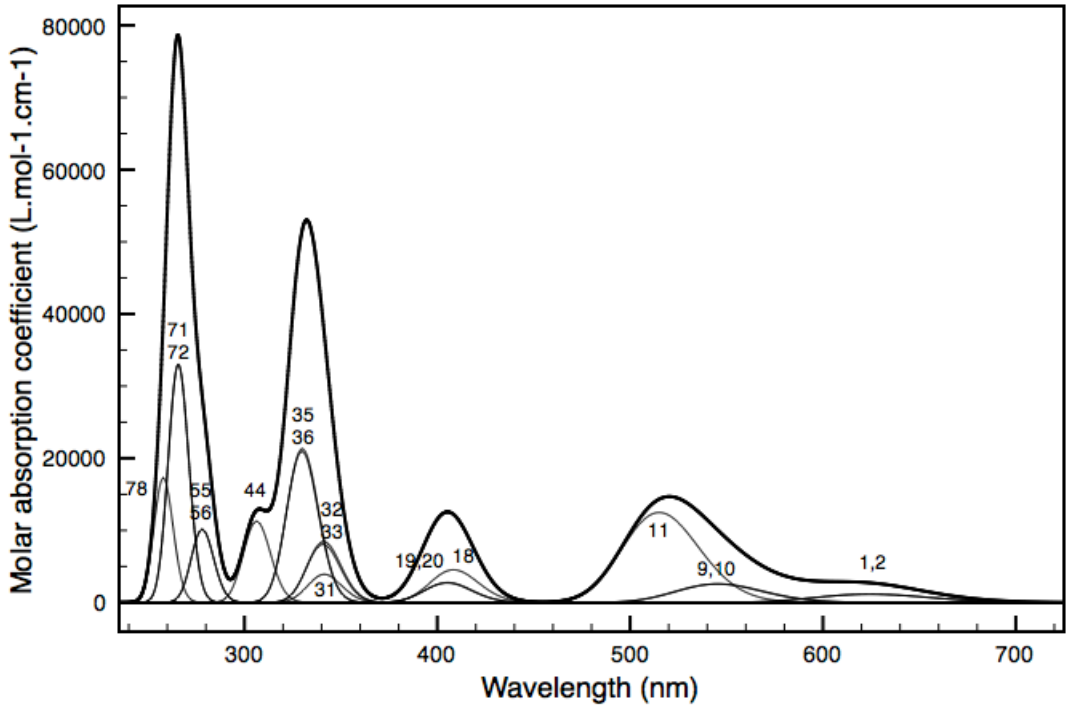
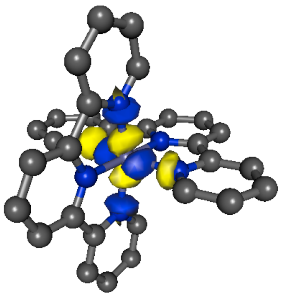
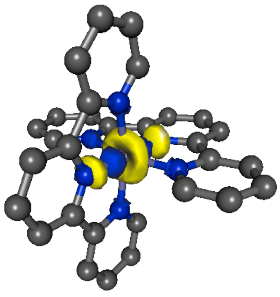


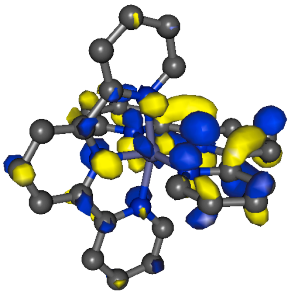
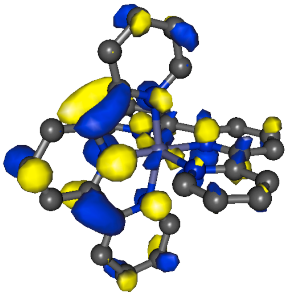
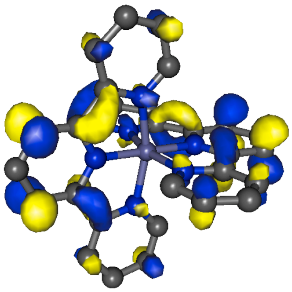
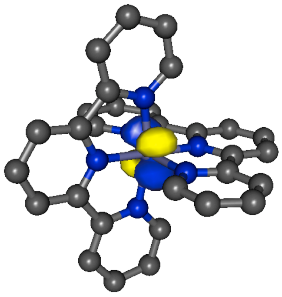
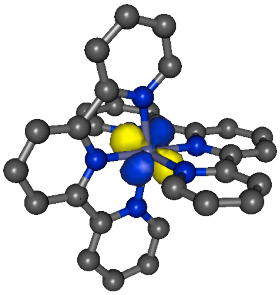
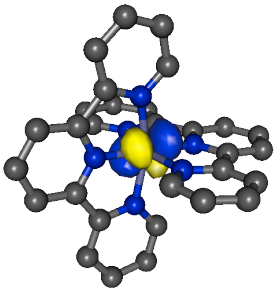
Table S2 : Main transitions found in the absorption spectrum

State	Oscillator strength	Wavelength (nm)	Main components	Major character
1	0.009465965	626.1	133 —> 134,135 Fe —> L_2	MLCT
2	0.009431728	625.2		
9	0.020960243	546.8	131,132 —> 137 Fe —> L_2	MLCT
10	0.020860162	545.8		
11	0.101252270	515.9	131 —> 134 132 —> 135	MLCT

			Fe —> L_2	
18	0.036833505	408.8	133 —> 139 Fe —> L_2	MLCT
19	0.022484406	405.8	133 —> 140,141 Fe —> L_2	MLCT
20	0.022042730	405.5		
31	0.031714153	341.6	131 —> 145 132 —> 144 133 —> 142,144 Fe —> L_2	MLCT
32	0.068576309	341.3	129 —> 134,135 133 —> 144,145 L_2 —> L_2 Fe —> L_2	LC MLCT
33	0.065430216	341.0		
35	0.172938106	330.2	133 —> 144,145 129,130 —> 134,135 L_2 —> L_2 Fe —> L_2	LC MLCT
36	0.169890068	330.0		
44	0.091286817	306.5	127,128 —> 135 129 —> 136 130 —> 137 131 —> 144 132 —> 145 L_2 —> L_2 Fe —> L_2	LC MLCT
55	0.082129823	278.2	129 —> 140,141 127,128 —> 136,137 L_2 —> L_2	LC
56	0.082315379	278.2		
71	0.268128801	265.9	127,128 —> 136,137 129 —> 140,141 L_2 —> L_2	LC
72	0.267478097	265.8		
78	0.140120099	258.0	124 —> 135 125 —> 134 126 —> 137 L_2 —> L_2	LC

Table S3 : Selected B3LYP* orbitals at the PBE0 geometry (eigenvalues in eV)

		
	LUMO+10 (-6.06)	LUMO+11 (-5.71)

		
LUMO (-7.95)	LUMO+1 (-7.94)	LUMO+2 (-7.84)
		
HOMO (-11.07)	HOMO-1 (-11.20)	HOMO-2 (-11.21)

4b. Data on Fe(tpy)(NCN)$^+$ (2) (E=-2745.640140461 a.u.)

Cartesian coordinates

Fe	5.432603	8.550271	4.748035
N	4.636839	6.758497	4.794284
N	5.239912	8.347768	6.621644
N	6.157269	10.276787	5.330696
N	3.678905	9.372318	4.306290
C	5.637505	8.750639	2.908230
N	7.258314	7.793899	4.532054
C	4.345140	5.995466	3.740906
H	4.584001	6.426891	2.776652
C	3.777691	4.739508	3.866879
H	3.559506	4.159423	2.979914
C	3.500586	4.250253	5.134681
H	3.058206	3.270551	5.265234
C	3.798132	5.036397	6.234089
H	3.596346	4.690922	7.239500
C	4.363849	6.285059	6.033756
C	4.720922	7.211803	7.106568
C	4.577705	7.026137	8.473099
H	4.155809	6.109887	8.864870
C	4.986535	8.044207	9.325299
H	4.882990	7.925647	10.396692
C	5.528860	9.213669	8.806973
H	5.853328	10.012072	9.461139
C	5.644480	9.335529	7.430731
C	6.181031	10.463741	6.672142
C	6.674681	11.625892	7.242384
H	6.680944	11.738577	8.319198
C	7.153826	12.628011	6.416886
H	7.545411	13.545609	6.838370
C	7.122945	12.435357	5.043901
H	7.485008	13.193043	4.361247
C	6.618186	11.247793	4.542728
H	6.572435	11.042693	3.480583
C	2.713813	9.650044	5.182163
H	2.927597	9.393968	6.213140
C	1.511220	10.227396	4.820551
H	0.763065	10.434499	5.574168
C	1.298538	10.529524	3.481965
H	0.368680	10.984001	3.161217
C	2.290972	10.244518	2.563553
H	2.163249	10.467096	1.511835
C	3.478945	9.665418	2.992624
C	4.613219	9.312533	2.152334
C	4.761607	9.473099	0.776853

H	3.973475	9.906442	0.169514
C	5.949796	9.067452	0.172543
H	6.072150	9.191455	-0.896616
C	6.984057	8.505193	0.918118
H	7.898254	8.198948	0.419979
C	6.819333	8.348929	2.292271
C	7.747974	7.788455	3.262574
C	9.010416	7.278045	2.986406
H	9.369935	7.288604	1.965546
C	9.780194	6.765237	4.013100
H	10.765514	6.362751	3.810891
C	9.271906	6.772427	5.305305
H	9.838164	6.380690	6.139644
C	8.010441	7.296668	5.513236
H	7.571400	7.324307	6.503910

Figure S4 : Computed UV-Vis absorption spectrum in the 285-1045 nm range.

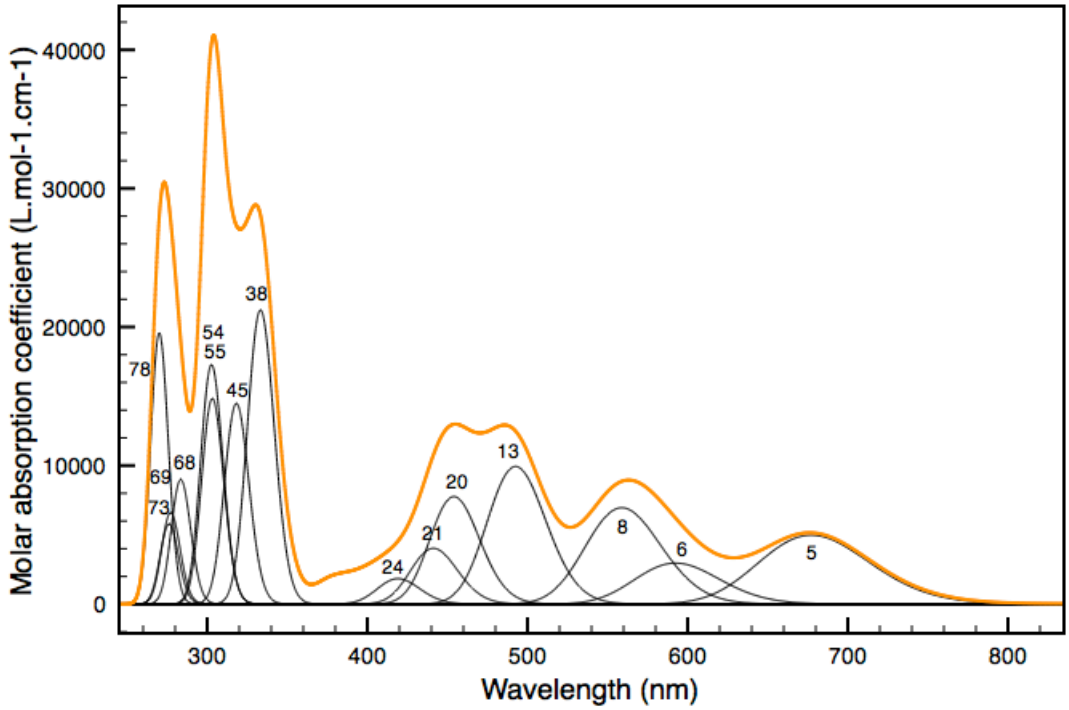


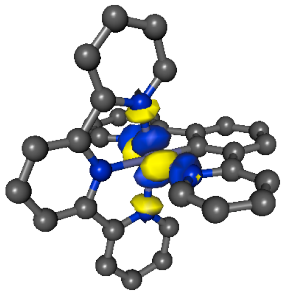
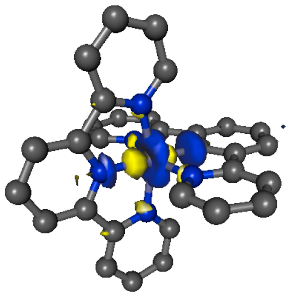
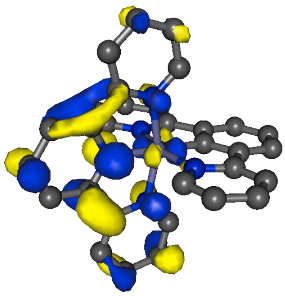
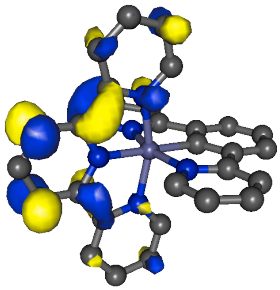
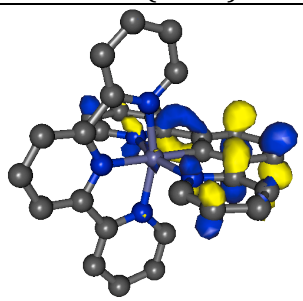
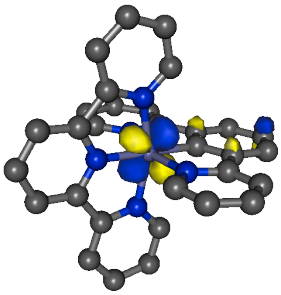
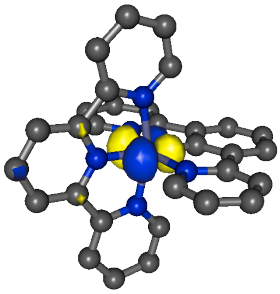
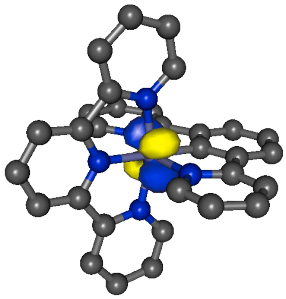
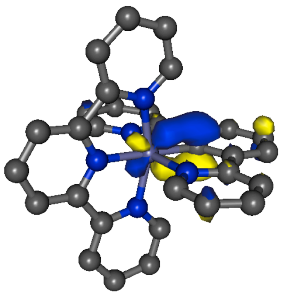
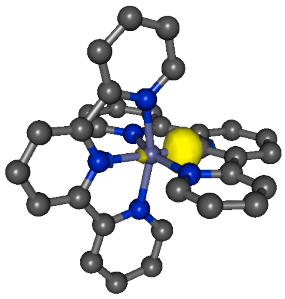
Table S4 : Main transitions found in the absorption spectrum (dpb = dipyridylbenzene)

State	Oscillator strength	Wavelength (nm)	Main components	Character
5	0.040383249	679.0	132 —> 135 131 —> 134 Fe —> tpy	MLCT
6	0.024031014	593.6	133 —> 136 Fe —> dpb	MLCT
8	0.056436143	559.9	131 —> 136	MLCT

			132 —> 134 Fe —> tpy Fe —> dpb	MLCT MLCT
13	0.080612033	493.3	131 —> 137 133 —> 138 Fe —> tpy Fe —> dpb	MLCT
20	0.062974349	454.6	131 —> 139 Fe —> tpy	MLCT
21	0.032671708	441.7	131 —> 138 131 —> 141 Fe —> tpy Fe —> dpb	MLCT MLCT
24	0.014936180	419.5	133 —> 142 130 —> 135 Fe —> tpy	MLCT
38	0.172342034	333.5	128 —> 134 126 —> 135 tpy —> tpy	LC(tpy)
45	0.117628177	318.4	129 —> 136,138 130 —> 137 FePh —> dpb FePh —> tpy dpb —> dpb	PBLCT LC(dpb)
54	0.140241435	302.9	128 —> 137 130 —> 136 126 —> 134 tpy —> dpb dpb —> dpb tpy —> tpy	LL’CT LC(dpb) LC(tpy)
55	0.120521925	303.4	128 —> 137 130 —> 136 tpy —> dpb dpb —> dpb	LL’CT LC(dpb)
68	0.073032113	283.6	126 —> 135 128 —> 139 tpy —> tpy	LC(tpy)
69	0.053672579	277.3	133 —> 145 124 —> 135 Fe —> dpb dpb+tpy —> tpy	MLCT LC(tpy)
73	0.046943079	276.3	124 —> 135 123 —> 134 dpb+tpy —> tpy NFeN+tpy —> tpy	LC(tpy)
78	0.158794162	270.2	133 —> 147 125 —> 136 130 —> 142	MLCT LC(dpb)

			Fe —> dpb dpb —> dpb	

Table S5 : Selected B3LYP* orbitals at the PBE0 geometry (eigenvalues in eV)

	 LUMO+9 (-2.78)	 LUMO+13 (-1.83)
 LUMO (-4.99)	 LUMO+1 (-4.98)	 LUMO+2 (-4.31)
 HOMO (-7.51)	 HOMO-1 (-7.65)	 HOMO-2 (-7.71)
	 HOMO-4 (-8.90)	 HOMO-5 (-9.20)

4c. Data on Fe(tpy)(NNC)$^+$ (3) (E=-2745.643566699 a.u.)

Cartesian coordinates

Fe	5.353748	8.591769	4.770837
N	4.598217	6.796601	4.780269
N	5.196143	8.375007	6.599418
N	6.110347	10.297512	5.324738
N	3.602921	9.418829	4.284204
N	5.587367	8.783352	2.890710
C	7.140707	7.836094	4.645842
C	4.330810	6.032111	3.721935
H	4.549058	6.473329	2.757630
C	3.819949	4.752912	3.836466
H	3.623003	4.172747	2.944637
C	3.575923	4.236910	5.101551
H	3.179361	3.236953	5.224214
C	3.853560	5.021593	6.205791
H	3.684438	4.655089	7.209726
C	4.363873	6.295854	6.015550
C	4.723540	7.216191	7.085866
C	4.651077	6.998584	8.452351
H	4.269223	6.062535	8.838041
C	5.086170	7.999469	9.310416
H	5.039180	7.852812	10.382124
C	5.595472	9.182700	8.792356
H	5.957064	9.965116	9.446281
C	5.643364	9.341308	7.416702
C	6.173244	10.471017	6.665701
C	6.718231	11.611730	7.233238
H	6.756893	11.710463	8.310700
C	7.212383	12.604008	6.406603
H	7.646904	13.502973	6.825791
C	7.146986	12.421929	5.032392
H	7.526275	13.168918	4.347373
C	6.591138	11.257507	4.535745
H	6.530289	11.064391	3.472486
C	2.609330	9.713422	5.119826
H	2.787380	9.473254	6.161535
C	1.423544	10.288152	4.698217
H	0.646410	10.510923	5.417582
C	1.261202	10.568157	3.349197
H	0.346446	11.019468	2.984847
C	2.288552	10.263132	2.473969
H	2.199001	10.468404	1.415251
C	3.448669	9.688989	2.970504
C	4.605628	9.319004	2.154894
C	4.735756	9.472550	0.785237

H	3.937235	9.902583	0.196231
C	5.922923	9.054268	0.192874
H	6.057725	9.160843	-0.876966
C	6.930785	8.502024	0.963671
H	7.858266	8.172029	0.515361
C	6.742894	8.369804	2.339117
C	7.649666	7.819987	3.328504
C	8.910848	7.309464	3.024052
H	9.273434	7.309286	2.001383
C	9.699276	6.799436	4.039152
H	10.680758	6.398194	3.818685
C	9.220858	6.804616	5.346584
H	9.840110	6.403772	6.142059
C	7.961898	7.316370	5.641312
H	7.621393	7.302489	6.673510

Figure S5 : Computed UV-Vis absorption spectrum in the 245-845 nm range.

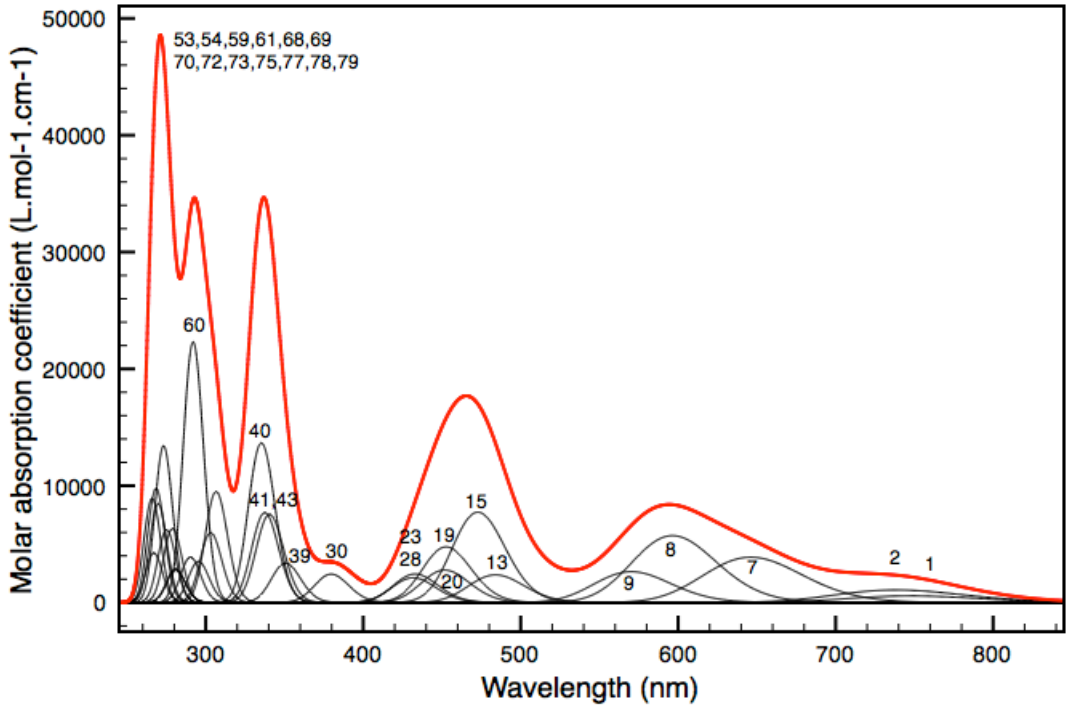


Table S6 : Main transitions found in the absorption spectrum (pbp = phenylbipyridine)

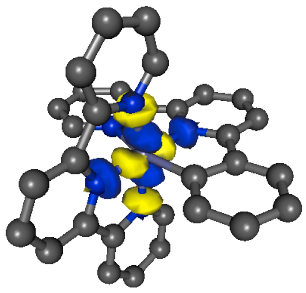
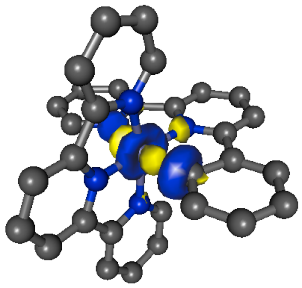
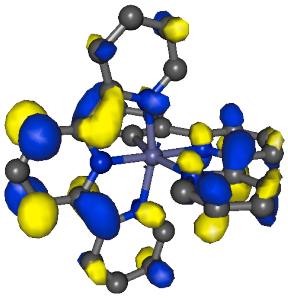
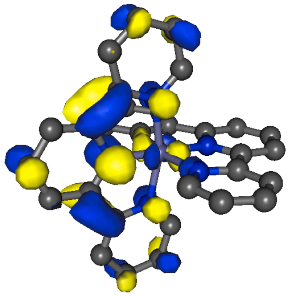
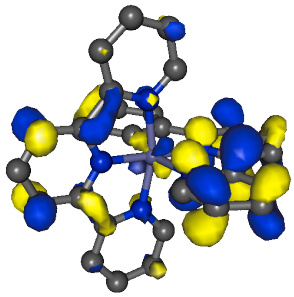
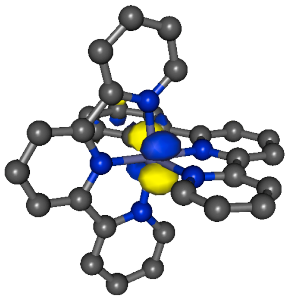
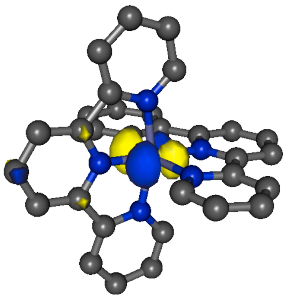
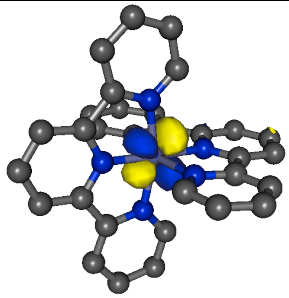
State	Oscillator strength	Wavelength (nm)	Main components	Major character
1	0.004613815	749.8	133 —> 134 Fe —> tpy	MLCT
2	0.008745396	740.7	133 —> 135 Fe —> tpy+pbp	MLCT
7	0.031482189	647.6	132 —> 135,136 Fe —> tpy+pbp	MLCT

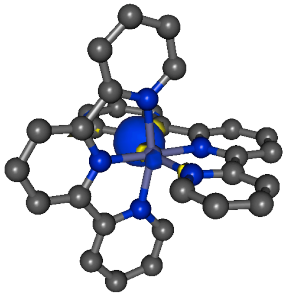
8	0.046458306	597.6	131 —> 135,136 Fe —> tpy+pbp	MLCT
9	0.021443859	571.3	133 —> 137 132 —> 134 Fe —> pbp Fe —> tpy	MLCT MLCT
13	0.019226835	484.7	133 —> 139 132 —> 138 Fe —> tpy Fe —> tpy+pbp	MLCT MLCT
15	0.062760310	473.4	133 —> 138 Fe —> tpy+pbp	MLCT
19	0.038658545	453.2	132 —> 140 133 —> 139 Fe —> tpy Fe —> tpy+pbp	MLCT MLCT
20	0.022556016	452.3	131 —> 138,140 Fe —> tpy+pbp	MLCT MLCT
23	0.019813633	433.4	130 —> 135,136 pbp —> tpy+pbp	LC(pbp)
28	0.017201843	432.2	129 —> 136 pbp —> tpy+pbp	LC(pbp)
30	0.019718522	380.0	132 —> 142 129 —> 135 133 —> 140,143 Fe —> pbp Fe —> tpy Fe —> tpy+pbp pbp —> tpy+pbp	MLCT LC(pbp)
39	0.027369354	351.0	130 —> 137,138 131 —> 143 pbp —> pbp pbp —> tpy+pbp Fe —> pbp	LC(pbp) MLCT
40	0.110933993	335.6	127 —> 134 130 —> 139 tpy —> tpy pbp —> tpy	LC(tpy) LL’CT
41	0.062475501	337.7	132 —> 142 130 —> 140 131 —> 143 Fe —> tpy pbp —> tpy Fe —> pbp	MLCT LL’CT
43	0.061275222	340.7	130 —> 139 127 —> 134 pbp —> tpy tpy —> tpy	LL’CT LC(tpy)
53	0.077141580	306.8	129 —> 140	LL’CT

			125 —> 134 133 —> 146 pbp —> tpy+pbp tpy —> tpy Fe —> tpy	LC(tpy) MLCT
54	0.048514790	303.3	125 —> 134 129 —> 138 131 —> 145 tpy —> tpy pbp —> pbp+tpy Fe —> pbp	LC(tpy) LC(pbp) MLCT
59	0.028552385	295.6	133 —> 146 Fe —> tpy	MLCT
60	0.181094703	292.1	133 —> 145 129 —> 138 Fe —> pbp pbp —> pbp+tpy	MLCT LC(pbp)
61	0.031572014	290.5	128 —> 139 127 —> 138 NFeC —> tpy tpy —> tpy+pbp	SBLCT LC(tpy)
68	0.022550169	281.1	131 —> 144 128 —> 140 127 —> 139 Fe —> FeN_3C NFeC —> tpy+pbp tpy —> tpy	MC SBLCT LC(tpy)
69	0.023443103	281.0	128 —> 139 127 —> 138 NFeC —> tpy tpy —> tpy+pbp	SBLCT LC(tpy)
70	0.051450119	279.1	127 —> 139 128 —> 140 tpy —> tpy NFeC —> tpy+pbp	LC(tpy) SBLCT
72	0.050552464	275.3	127 —> 140 126 —> 137 tpy —> tpy+pbp pbp —> pbp	LC(tpy) LC(pbp)
73	0.108868863	273.4	126 —> 137 133 —> 147 127 —> 140 pbp —> pbp Fe —> pbp tpy —> tpy+pbp	LC(pbp) MLCT LC(tpy)
75	0.068593025	269.9	129 —> 141 133 —> 148 124 —> 134 pbp —> FeN_4	LMCT MLCT LC(tpy)

			Fe —> tpy pbp+tpy —> tpy	
77	0.034407211	267.2	133 —> 148 132 —> 147 Fe —> tpy Fe —> pbp	MLCT
78	0.072268722	266.1	133 —> 147 126 —> 140 126 —> 135,136,137 Fe —> pbp pbp —> pbp+tpy pbp —> pbp	MLCT LL'CT LC(pbp)
79	0.079316812	268.6	129 —> 141 124 —> 134 133 —> 148 pbp —> FeN_4 pbp+tpy —> tpy Fe —> tpy	LMCT LC(tpy) MLCT

Table S7 : Selected B3LYP* orbitals at the PBE0 geometry (eigenvalues in eV)

	 LUMO+9 (-2.49)	 LUMO+12 (-2.11)
 LUMO (-4.92)	 LUMO+1 (-4.88)	 LUMO+2 (-4.85)
 HOMO (-7.49)	 HOMO-1 (-7.67)	 HOMO-2 (-7.89)

	 HOMO-5 (-9.10)	

4d. Data on Fe(tpy)(CNC) (4) (E=-2729.110301919 a.u.)

Cartesian coordinates

Fe	5.428482	8.550449	4.821167
N	4.649703	6.789930	4.815476
N	5.244720	8.351525	6.610136
N	6.147211	10.252837	5.353106
C	3.692839	9.363927	4.383336
N	5.640243	8.756440	2.897334
C	7.233577	7.797615	4.604092
C	4.364750	6.037737	3.747725
H	4.605172	6.481551	2.790430
C	3.803699	4.782685	3.850157
H	3.593896	4.216902	2.951768
C	3.518421	4.267734	5.112080
H	3.079084	3.284115	5.222399
C	3.805318	5.036264	6.220815
H	3.600654	4.678823	7.221807
C	4.369706	6.293849	6.045903
C	4.720329	7.209180	7.109760
C	4.574973	7.029261	8.474021
H	4.149192	6.109817	8.855420
C	4.978625	8.042165	9.335720
H	4.870240	7.922563	10.406265
C	5.523142	9.209338	8.813253
H	5.847618	10.011780	9.463286
C	5.646787	9.339608	7.441179
C	6.178395	10.457342	6.693495
C	6.675923	11.630606	7.247269
H	6.684632	11.750599	8.323623
C	7.149869	12.620842	6.412302
H	7.543971	13.543883	6.819562
C	7.110908	12.408765	5.036651
H	7.468960	13.157962	4.342344
C	6.605469	11.220557	4.553024
H	6.554625	11.008317	3.493352
C	2.640140	9.678503	5.241708
H	2.734801	9.468546	6.304412
C	1.466614	10.255391	4.770000
H	0.663248	10.492185	5.461211
C	1.309025	10.536972	3.414809
H	0.392201	10.988500	3.053303
C	2.332802	10.235287	2.534068
H	2.220400	10.451598	1.475897
C	3.505411	9.657703	3.018328
C	4.639240	9.299082	2.181859
C	4.763896	9.455795	0.804782

H	3.953062	9.890063	0.235251
C	5.936966	9.044618	0.190956
H	6.055080	9.159280	-0.881113
C	6.959692	8.486152	0.941903
H	7.882274	8.158043	0.482281
C	6.782669	8.349838	2.315517
C	7.715755	7.790108	3.280540
C	8.970646	7.282542	2.947347
H	9.311790	7.289558	1.916719
C	9.781727	6.766132	3.942939
H	10.759361	6.367110	3.698560
C	9.330347	6.762207	5.260864
H	9.966607	6.357123	6.041878
C	8.077189	7.271175	5.581296
H	7.751737	7.253542	6.618909

Figure S6 : Computed UV-Vis absorption spectrum in the 255-1045 nm range.

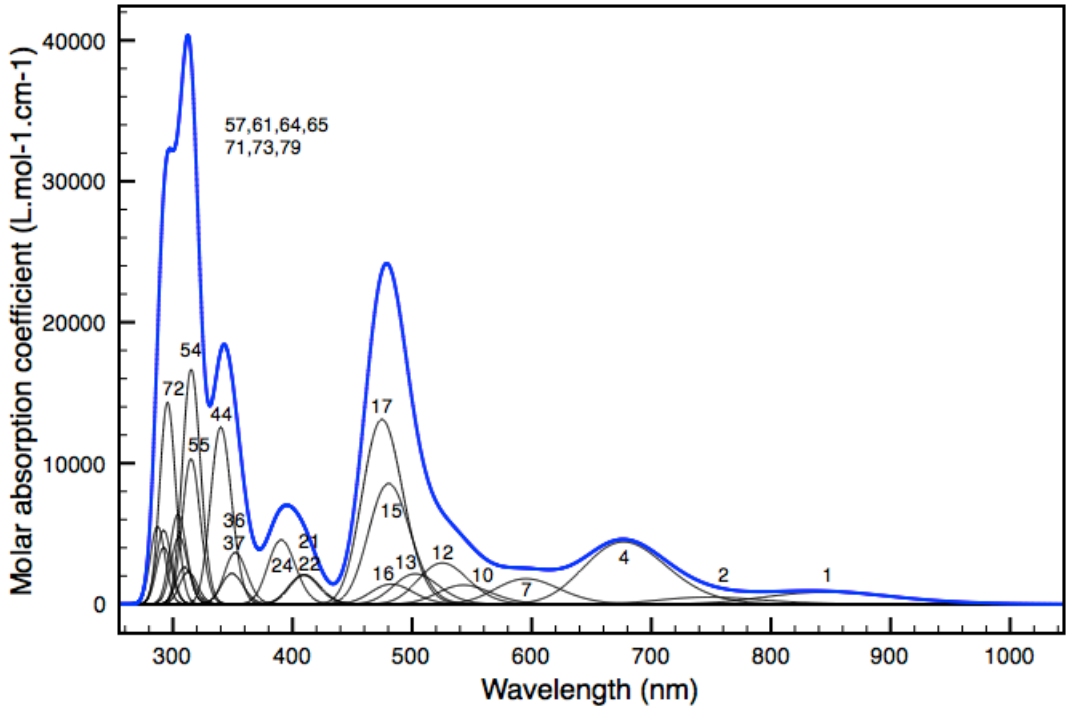


Table S8 : Main transitions found in the absorption spectrum (dpp = diphenylpyridine)

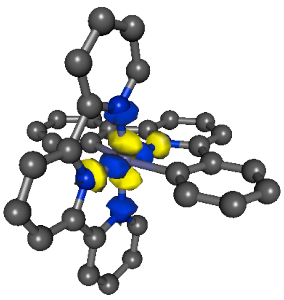
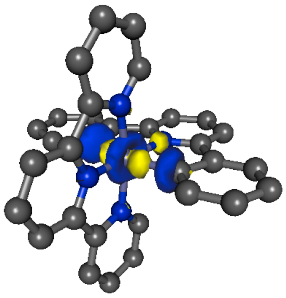
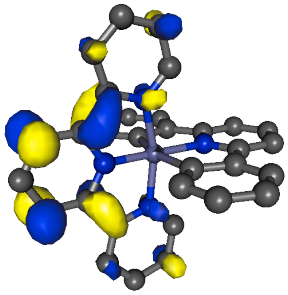
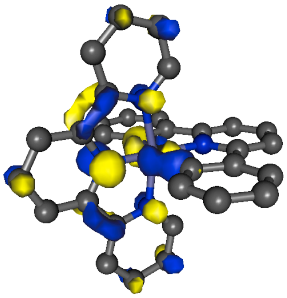
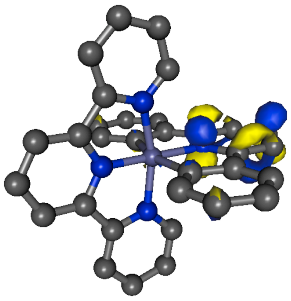
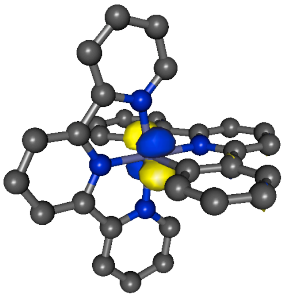
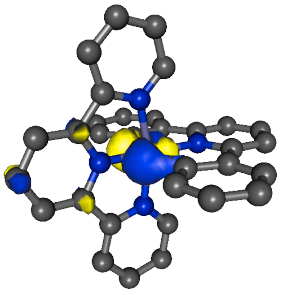
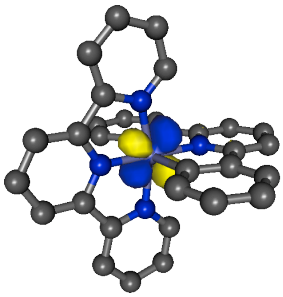
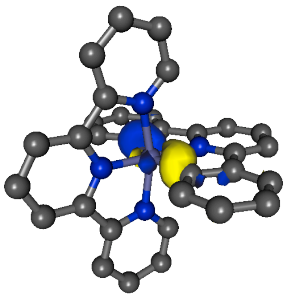
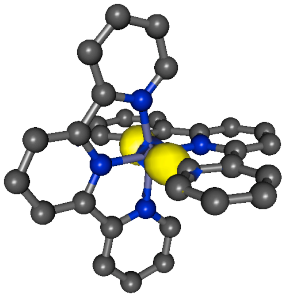
State	Oscillator strength	Wavelength (nm)	Main components	Major character
1	0.006907673	849.4	133 —> 134 Fe —> tpy	MLCT
2	0.004034654	750.2	132 —> 134 133 —> 135 Fe —> tpy	MLCT
4	0.035832869	678.6	133 —> 135	MLCT

			132 —> 134 Fe —> tpy	
7	0.014604839	596.4	133 —> 137 132 —> 135 Fe —> tpy Fe —> dpp	MLCT
10	0.010971396	543.8	133 —> 139 132 —> 135 Fe —> tpy	MLCT
12	0.023694015	526.1	133 —> 138 132 —> 139 Fe —> tpy	MLCT
13	0.017414341	503.3	132 —> 138 Fe —> tpy	MLCT
15	0.069434371	481.0	131 —> 136,139 133 —> 139 Fe —> dpp Fe —> tpy	MLCT
16	0.011515283	483.2	131 —> 139 Fe —> tpy	MLCT
17	0.106311320	475.4	132-139 133-138 Fe —> tpy	MLCT
21	0.016873155	410.5	132,133 —> 140 Fe —> tpy	MLCT
22	0.016799837	409.3	132,133 —> 140 Fe —> tpy	MLCT
24	0.036968800	390.9	130 —> 135 CFeC —> tpy	SBLCT
36	0.029686634	352.4	131 —> 142 132 —> 140 125 —> 134 130 —> 138 Fe —> dpp Fe —> tpy tpy —> tpy CFeC —> tpy	MLCT LC(tpy) SBLCT
37	0.017672544	349.5	129 —> 136 132 —> 141 dpp —> dpp Fe —> FeN_4	LC(dpp) MC
44	0.101928399	340.2	130-138 133-143 129-137 129-139 CFeC —> tpy Fe —> dpp dpp —> dpp dpp —> tpy	SBLCT MLCT LC(dpp) LL’CT

54	0.135275569	315.5	125-135 124-134 tpy —> tpy	LC(tpy)
55	0.083612168	315.3	128-139 131-143 128-137 126-137 dpp —> tpy Fe —> dpp dpp —> dpp	LL'CT MLCT LC(dpp)
57	0.018562980	312.9	131-144 126-136 127-137 133-147 Fe —> dpp dpp —> dpp Fe —> tpy	MLCT LC(dpp)
61	0.021217572	309.9	133-147 127-137 125-137 Fe —> tpy dpp —> dpp tpy —> dpp	MLCT LC(dpp) LL'CT
64	0.038692897	305.4	128-139 125-136 132-146 128-137 dpp —> tpy tpy —> dpp Fe —> FeC_2 dpp —> dpp	LL'CT MC LC(dpp)
65	0.051643093	304.3	127-139 125-137 127-137 133-143 dpp —> tpy tpy —> dpp dpp —> dpp Fe —> dpp	LL'CT LC(dpp) MLCT
71	0.042498768	292.4	130-140 124-135 125-134 CFeC —> tpy tpy —> tpy	SBLCT LC(tpy)
72	0.116149447	295.6	126-137 126-139 dpp —> dpp dpp —> tpy	LC(dpp) LL'CT
73	0.032601315	292.5	127-139	LL'CT

			130-140 dpp —> tpy CFeC —> tpy	SBLCT
79	0.044652682	287.3	126-139 dpp —> tpy	LL'CT

Table S9 : Selected B3LYP* orbitals at the PBE0 geometry (eigenvalues in eV)

	 LUMO+9 (+0.61)	 LUMO+13 (+1.13)
 LUMO (-1.99)	 LUMO+1 (-1.69)	 LUMO+2 (-1.26)
 HOMO (-4.34)	 HOMO-1 (-4.39)	 HOMO-2 (-4.83)
	 HOMO-3 (-5.49)	 HOMO-9 (-7.03)

4e. Data on $Fe(NCN)_2$ (5) (E=-2729.095831640 a.u.)

Cartesian coordinates

Fe	6.261836	3.128757	5.140752
N	6.964702	1.309367	4.788797
C	6.262468	3.131229	3.260527
C	7.310098	0.428328	5.728125
C	7.809368	-0.828756	5.438259
C	7.957326	-1.195091	4.106661
C	7.601077	-0.292819	3.122704
C	7.106574	0.957495	3.478347
C	6.699457	2.007697	2.557126
C	6.706958	2.002027	1.165092
C	6.274239	3.138768	0.481331
N	8.082612	3.831927	5.488532
C	6.263391	3.131004	7.020977
C	8.962183	4.176493	4.547502
C	10.219954	4.675467	4.834905
C	10.588749	4.824061	6.165725
C	9.688048	4.468727	7.151442
C	8.436942	3.974485	6.798253
C	7.388432	3.568215	7.721791
C	7.397016	3.576386	9.113785
C	6.261654	3.144167	9.800177
H	7.173361	0.768292	6.747824
H	8.075782	-1.499978	6.244284
H	8.347166	-2.171218	3.841823
H	7.701235	-0.536473	2.072214
H	7.042112	1.135197	0.602355
H	6.278893	3.141751	-0.602687
H	8.620756	4.039436	3.528343
H	10.889812	4.941137	4.027499
H	11.565504	5.213656	6.428600
H	9.933538	4.569319	8.201453
H	8.265060	3.911752	9.674517
H	6.260962	3.149375	10.884196
N	5.558011	4.949200	4.792769
C	5.207127	5.826406	5.733663
C	4.707996	7.084069	5.446086
C	4.566514	7.455524	4.115222
C	4.928109	6.557153	3.129653
C	5.421462	5.305742	3.482999
C	5.832164	4.258839	2.559582
C	5.836204	4.271977	1.167607
H	5.506847	5.142281	0.606823
H	4.832727	6.804530	2.079602
H	4.177386	8.432421	3.852196

H	4.437081	7.751935	6.253392
H	5.339370	5.483245	6.752874
N	4.442753	2.425305	5.492911
C	3.564052	2.073674	4.553717
C	2.307019	1.574389	4.843757
C	1.937995	1.433611	6.175399
C	2.837962	1.796045	7.159212
C	4.088641	2.289512	6.803409
C	5.137261	2.700993	7.724511
C	5.127033	2.705719	9.116532
H	4.257916	2.376636	9.679320
H	2.592397	1.701158	8.209741
H	0.961678	1.044356	6.440388
H	1.637766	1.302794	4.037831
H	3.905770	2.205553	3.533965

Figure S7 : Computed UV-Vis absorption spectrum in the 265-935 nm range.

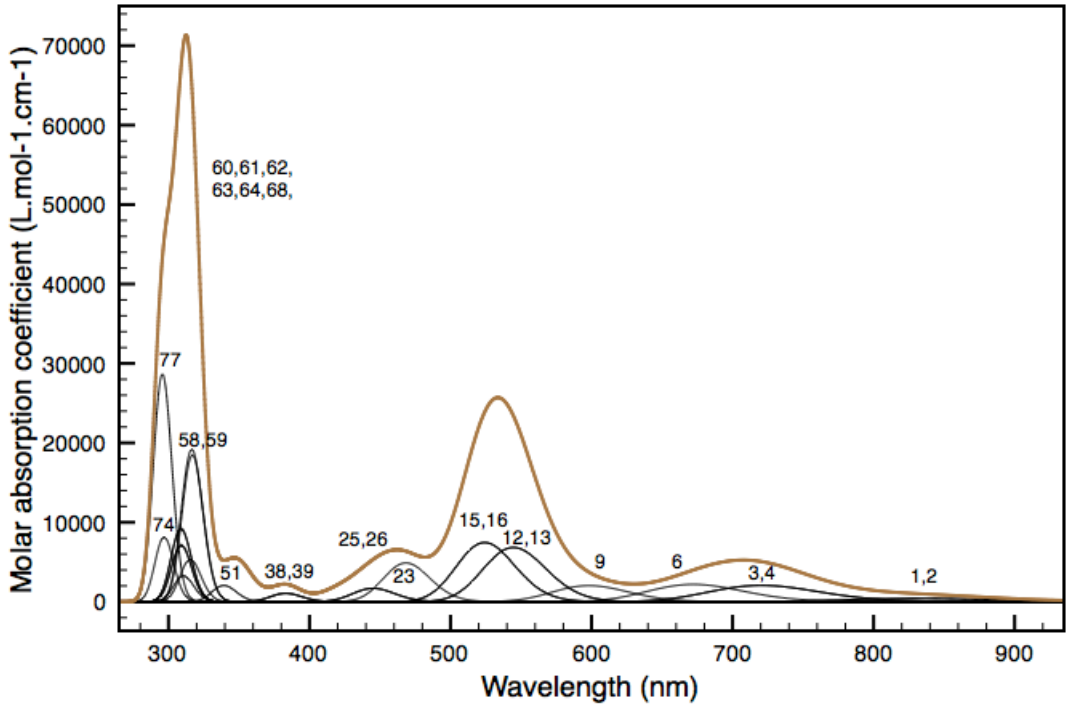


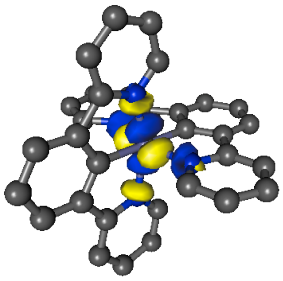
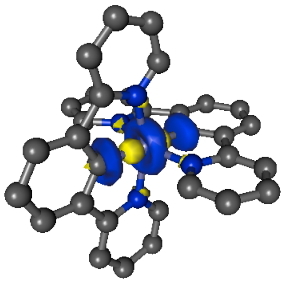
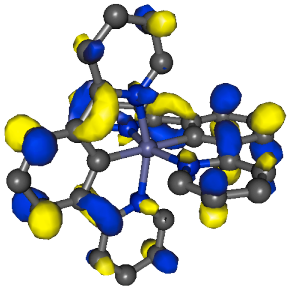
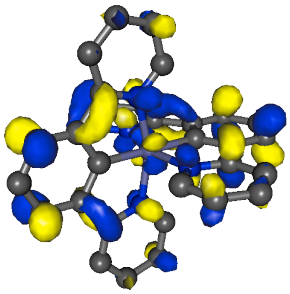
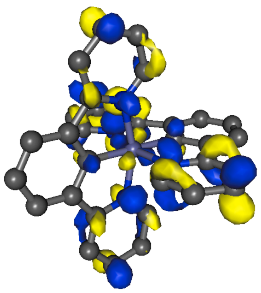
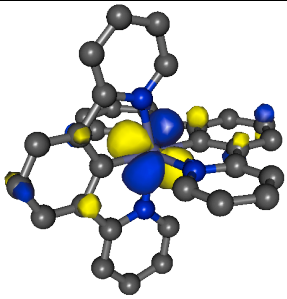
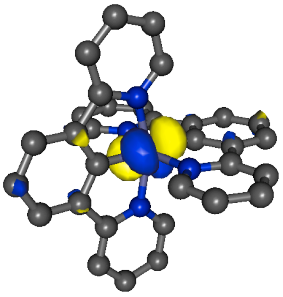
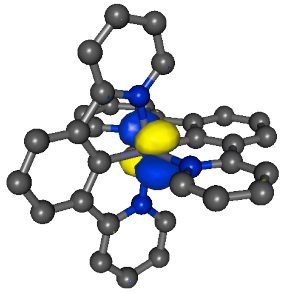
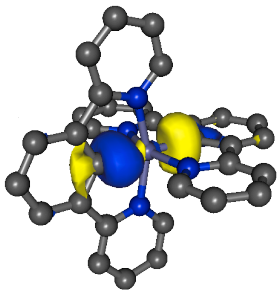
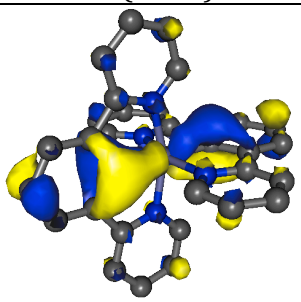
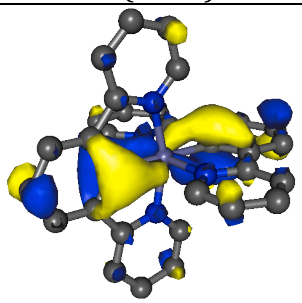
Table S10 : Main transitions found in the absorption spectrum

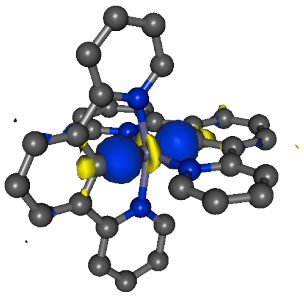
State	Oscillator strength	Wavelength (nm)	Main components	Major character
1	0.003339154	834.9	132,133 —> 134	MLCT
2	0.003351066	834.6	Fe —> L_2	
3	0.016697299	722.5	132,133 —> 135	MLCT
4	0.016709556	722.5	Fe —> L_2	
6	0.017735220	673.8	131 —> 134	MLCT

			Fe —> L_2	
9	0.016473785	599.3	132 —> 136 133 —> 137 Fe —> L	MLCT
12	0.055384742	545.5	131 —> 136,137 132,133 —> 139 Fe —> L Fe —> L_2	MLCT
13	0.055455557	545.5		
15	0.060483576	525.0	132,133 —> 139 131 —> 136,137 132,133 —> 142 Fe —> L Fe —> L_2 Fe —> FeN_4	MLCT MC
16	0.060458629	525.0		
23	0.039627264	469.0	131 —> 138 132 —> 140 133 —> 141 Fe —> L Fe —> L_2	MLCT
25	0.013709774	445.6	131 —> 140,141 Fe —> L	MLCT
26	0.013707664	445.6		
38	0.008598915	383.2	132,133 —> 143 126,127 —> 134 126,127 —> 135 Fe —> FeC_2 FePh —> L_2	PBLCT MC
39	0.008599517	383.7		
51	0.016621968	339.5	133 —> 145 132 —> 144 128 —> 134 129 —> 135 Fe —> L L_2 —> L_2	MLCT LC
58	0.149818096	317.1	126,127 —> 138 128 —> 136,137 FePh —> L_2 L_2 —> L_2	PBLCT LC
59	0.155722166	316.7		
60	0.043119389	315.6	128 —> 138 129 —> 139 L_2 —> L_2	LC
61	0.075216945	309.0	132,133 —> 146 126,127 —> 138 Fe —> FeC_2 FePh —> L_2	MC PBLCT
62	0.073846883	309.0		
63	0.056966124	309.2	132,133 —> 146 126,127 —> 138 Fe —> FeC_2 FePh —> L_2	MC PBLCT
64	0.058240536	309.3		
68	0.026318307	310.8	133 —> 150 132 —> 149	MLCT

			Fe —> L_2	
74	0.066003331	297.1	129 —> 139 L_2 —> L_2	LC
77	0.232652751	295.9	128 —> 138 129 —> 139 L_2 —> L_2	LC

Table S11 : Selected B3LYP* orbitals at the PBE0 geometry (eigenvalues in eV)

	 LUMO+8 (+0.46)	 LUMO+17 (+1.43)
 LUMO (-1.55)	 LUMO+1 (-1.44)	 LUMO+2 (-1.22)
 HOMO (-4.13)	 HOMO-1 (-4.13)	 HOMO-2 (-4.36)
 HOMO-3 (-5.04)	 HOMO-6 (-5.85)	 HOMO-7 (-5.85)

	 HOMO-8 (-7.14)	

4f. Data on Fe(NCN)(NNC) (6) (E=-2729.105131394 a.u.)

Cartesian coordinates

Fe	5.482925	8.534531	4.785217
N	4.659046	6.748766	4.822830
C	5.276950	8.340130	6.601390
N	6.182411	10.274813	5.371877
C	3.753770	9.333340	4.419797
N	5.677578	8.743749	2.889424
N	7.293443	7.786694	4.524192
C	4.356254	6.014496	3.751749
H	4.602332	6.462016	2.796276
C	3.759666	4.770913	3.832454
H	3.535590	4.221933	2.927211
C	3.456177	4.258929	5.088700
H	2.987137	3.287395	5.190422
C	3.755608	5.012699	6.206195
H	3.529223	4.656912	7.203533
C	4.355850	6.258646	6.057942
C	4.711782	7.173287	7.125318
C	4.537030	7.027735	8.497761
H	4.090242	6.130864	8.917682
C	4.934389	8.060006	9.347342
H	4.795561	7.953490	10.416853
C	5.499968	9.230615	8.841787
H	5.792160	10.022326	9.525588
C	5.668323	9.364936	7.467540
C	6.196375	10.488221	6.718139
C	6.665560	11.685735	7.247797
H	6.661655	11.819905	8.322844
C	7.117782	12.679402	6.402033
H	7.484078	13.617875	6.801779
C	7.088374	12.457345	5.030223
H	7.421740	13.209350	4.326844
C	6.612553	11.245757	4.566015
H	6.559127	11.027814	3.506457
C	2.699571	9.648772	5.281083
H	2.807359	9.436312	6.340591
C	1.523397	10.222805	4.818426
H	0.725573	10.456632	5.517122
C	1.349953	10.507410	3.463902
H	0.428457	10.957115	3.112070
C	2.365719	10.209650	2.575977
H	2.244357	10.426912	1.518643
C	3.545780	9.633681	3.049484
C	4.661404	9.287284	2.189373
C	4.784156	9.442902	0.810828

H	3.969416	9.875772	0.244923
C	5.952498	9.037932	0.181297
H	6.058409	9.156529	-0.890909
C	6.987362	8.479267	0.920452
H	7.905548	8.156022	0.448394
C	6.807933	8.346523	2.290302
C	7.751631	7.782634	3.249919
C	9.001010	7.274309	2.920808
H	9.328906	7.288263	1.889449
C	9.802739	6.756049	3.920251
H	10.780612	6.352862	3.686460
C	9.329316	6.761318	5.226920
H	9.921206	6.365692	6.042175
C	8.076125	7.284265	5.482672
H	7.654721	7.314481	6.480657

Figure S8 : Computed UV-Vis absorption spectrum in the 255-1045 nm range.

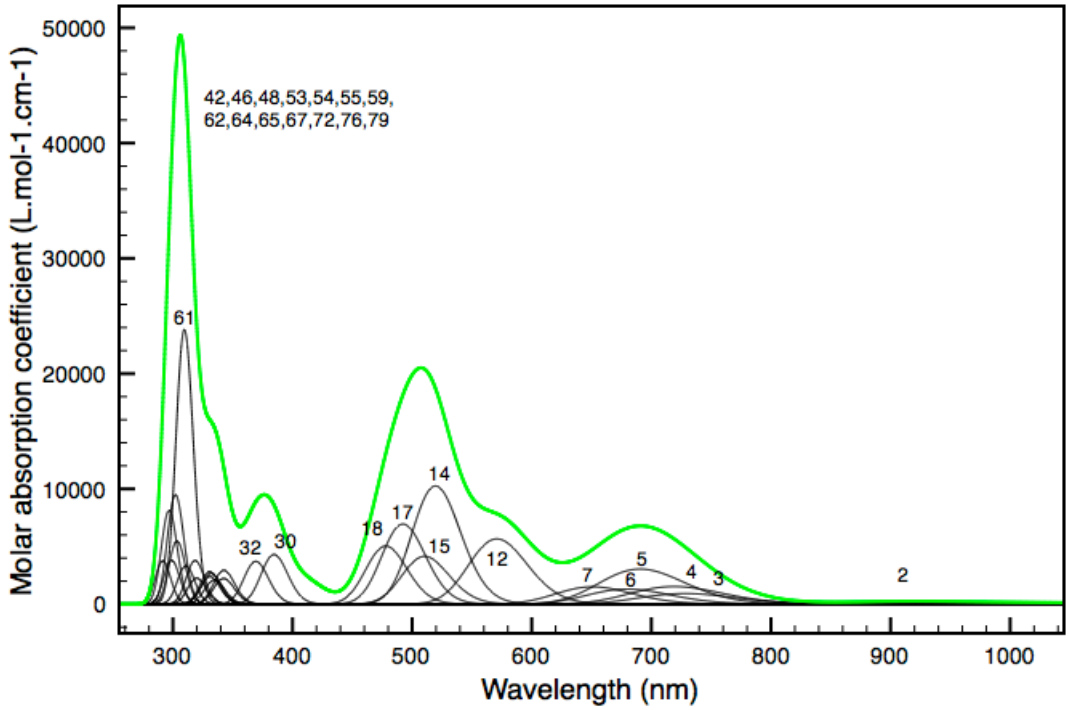


Table S12 : Main transitions found in the absorption spectrum (pbp = phenylbipyridine ; dpb = dipyridylbenzene)

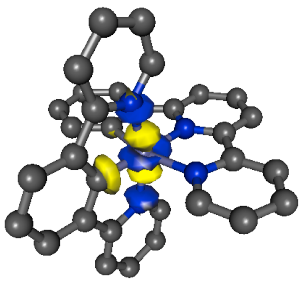
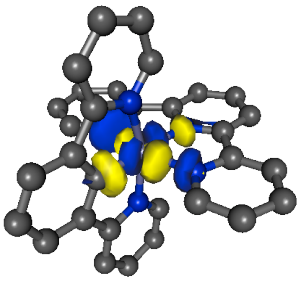
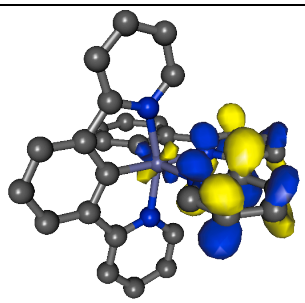
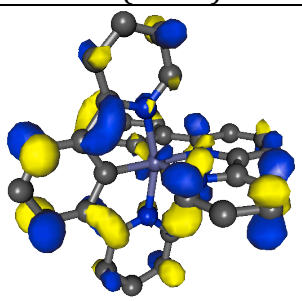
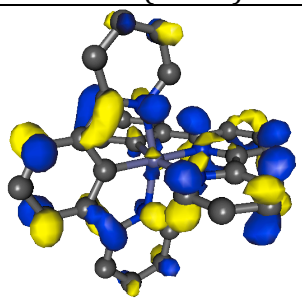
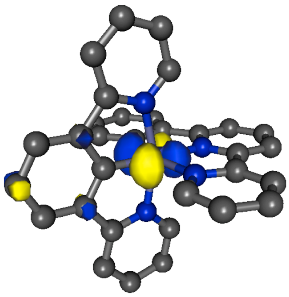
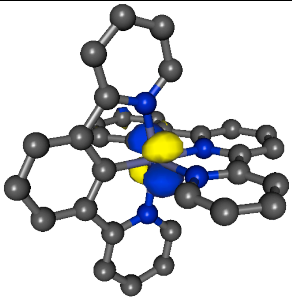
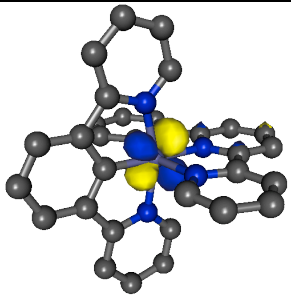
State	Oscillator strength	Wavelength (nm)	Main components	Major character
2	0.001887981	918.5	132 —> 134 Fe —> pbp	MLCT
3	0.007459227	730.4	133 —> 135,136 Fe —> dpb	MLCT

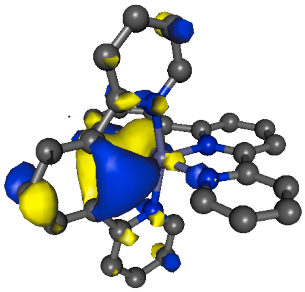
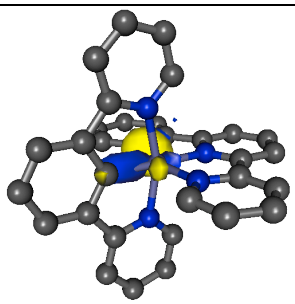
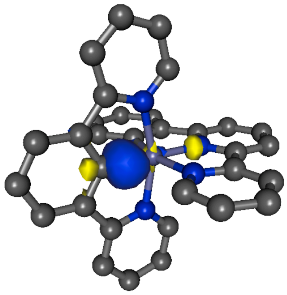
			Fe —> pbp	
4	0.012403493	721.1	131 —> 134,135 132 —> 135 Fe —> dpb Fe —> pbp	MLCT
5	0.024669670	692.5	132 —> 135 131 —> 134 Fe —> dpb Fe —> pbp	MLCT
6	0.010568684	681.5	133 —> 135,136 Fe —> dpb Fe —> pbp	MLCT
7	0.012205526	652.5	131 —> 134,135,136 132 —> 136 Fe —> dpb Fe —> pbp	MLCT
12	0.045924423	571.9	131,132 —> 137 133 —> 139 Fe —> dpb	MLCT
14	0.083188730	520.3	133 —> 139 132 —> 137 Fe —> dpb	MLCT
15	0.033646257	511.3	131 —> 138,139 Fe —> dpb Fe —> pbp	MLCT
17	0.056338350	493.0	132 —> 138,139 131 —> 139 133 —> 140 Fe —> pbp Fe —> dpb	MLCT
18	0.040879241	478.6	133 —> 140 132 —> 138 Fe —> dpb Fe —> pbp	MLCT
30	0.034909884	384.9	127 —> 134 131 —> 141 pbp —> pbp Fe —> pbp	LC(pbp) MLCT
32	0.030071183	369.6	132 —> 141 130 —> 136 133 —> 145 Fe —> pbp pbp —> pbp Fe —> dpb	MLCT LC(pbp)
42	0.018027727	342.7	131,132 —> 143 129,130 —> 136 Fe —> pbp dpb —> pbp pbp —> pbp	MLCT LL'CT LC(pbp)

46	0.023826385	342.8	130 —> 138 132 —> 143 pbp —> pbp Fe —> pbp	LC(pbp) MLCT
48	0.021762987	332.4	131 —> 143 133 —> 145 Fe —> pbp Fe —> dpb	MLCT
53	0.019424046	331.3	127 —> 137 129 —> 138 125 —> 136 pbp —> dpb dpb —> pbp CFeC —> pbp	LL'CT SBLCT
54	0.017018534	334.9	129 —> 138 127 —> 136,137 dpb —> pbp pbp —> pbp pbp —> dpb	LL'CT LC(pbp)
55	0.022810469	330.9	127 —> 136 133 —> 146 pbp —> pbp Fe —> FeN_2C_2	LC(pbp) MC
59	0.030672687	318.7	126 —> 137 CFeC —> dpb	SBLCT
61	0.193331562	309.7	129 —> 137 127 —> 137 128 —> 135 130 —> 140 dpb —> dpb pbp —> dpb PhFe —> dpb	LC(dpb) LL'CT PBLCT
62	0.026947823	311.0	125 —> 137 CFeC —> dpb	SBLCT
64	0.044436714	303.5	127 —> 138 129 —> 136 130 —> 138 132 —> 143 pbp —> pbp dpb —> pbp Fe —> pbp	LC(pbp) LL'CT MLCT
65	0.018302203	320.0	133 —> 148 Fe —> pbp	MLCT
67	0.077096575	302.3	127 —> 138 129 —> 135 pbp —> pbp dpb —> dpb	LC(pbp) LC(dpb)

72	0.066043611	297.0	132 —> 147 127 —> 138 Fe —> pbp pbp —> pbp	MLCT LC(pbp)
76	0.030886227	299.0	128 —> 139 129,130 —> 140 131 —> 146,148 PhFe —> dpb dpb —> dpb pbp —> dpb Fe —> FeN_2C_2 Fe —> pbp	PBLCT LC(dpb) LL'CT MC MLCT
79	0.030431359	291.7	131 —> 147 124 —> 135 Fe —> pbp pbp —> dpb	MLCT LL'CT

Table S13 : Selected B3LYP* orbitals at the PBE0 geometry (eigenvalues in eV)

	 LUMO+9 (+0.65)	 LUMO+11 (+0.82)
 LUMO (-1.96)	 LUMO+1 (-1.51)	 LUMO+2 (-1.38)
 HOMO (-4.13)	 HOMO-1 (-4.22)	 HOMO-2 (-4.35)

		
HOMO-5 (-5.84)	HOMO-7 (-6.01)	HOMO-8 (-6.16)

4g. Data on $Fe(NNC)_2$ (7) (E=-2729.109767954 a.u.)

Cartesian coordinates

Fe	5.478079	8.459160	4.744803
N	4.633984	6.692934	4.814058
N	5.275189	8.285453	6.601165
C	6.146285	10.198735	5.237859
C	3.776881	9.305579	4.418737
N	5.667434	8.689164	2.894062
N	7.293589	7.763788	4.517122
C	4.294454	5.938007	3.765826
H	4.537019	6.356106	2.796173
C	3.667495	4.715207	3.897491
H	3.411977	4.145541	3.013410
C	3.372273	4.243601	5.172133
H	2.880848	3.288247	5.309026
C	3.709547	5.021870	6.262493
H	3.489101	4.699150	7.271778
C	4.336374	6.243151	6.055384
C	4.710626	7.177733	7.106038
C	4.505791	7.024544	8.469507
H	4.041549	6.128033	8.858854
C	4.896695	8.058673	9.308834
H	4.744719	7.974328	10.378489
C	5.468073	9.205485	8.777277
H	5.762795	10.028513	9.415373
C	5.648910	9.307394	7.401496
C	6.179423	10.414821	6.635582
C	6.656932	11.597361	7.200624
H	6.666199	11.728350	8.279193
C	7.118052	12.605999	6.376101
H	7.492230	13.531542	6.798073
C	7.090671	12.423570	4.992781
H	7.445136	13.219578	4.344634
C	6.613719	11.244352	4.439128
H	6.597441	11.138004	3.357704
C	2.746806	9.631632	5.303699
H	2.870595	9.427039	6.363812
C	1.570527	10.221182	4.863351
H	0.789706	10.466993	5.576849
C	1.376381	10.510152	3.512069
H	0.455406	10.974581	3.178936
C	2.372857	10.204053	2.604935
H	2.237839	10.428866	1.550929
C	3.551992	9.610968	3.056070
C	4.666082	9.270019	2.197952
C	4.812268	9.485955	0.831272

H	4.007983	9.951838	0.276716
C	5.991338	9.114101	0.202602
H	6.116836	9.284256	-0.860314
C	7.016937	8.535595	0.937552
H	7.952585	8.252878	0.474078
C	6.816975	8.339572	2.296333
C	7.766673	7.786633	3.249415
C	9.041427	7.336160	2.933557
H	9.380395	7.371808	1.906371
C	9.855407	6.854012	3.940401
H	10.853855	6.498064	3.717789
C	9.369230	6.841334	5.243413
H	9.973111	6.481126	6.066242
C	8.091435	7.304317	5.484665
H	7.669683	7.324910	6.482579

Figure S9 : Computed UV-Vis absorption spectrum in the 265-885 nm range.

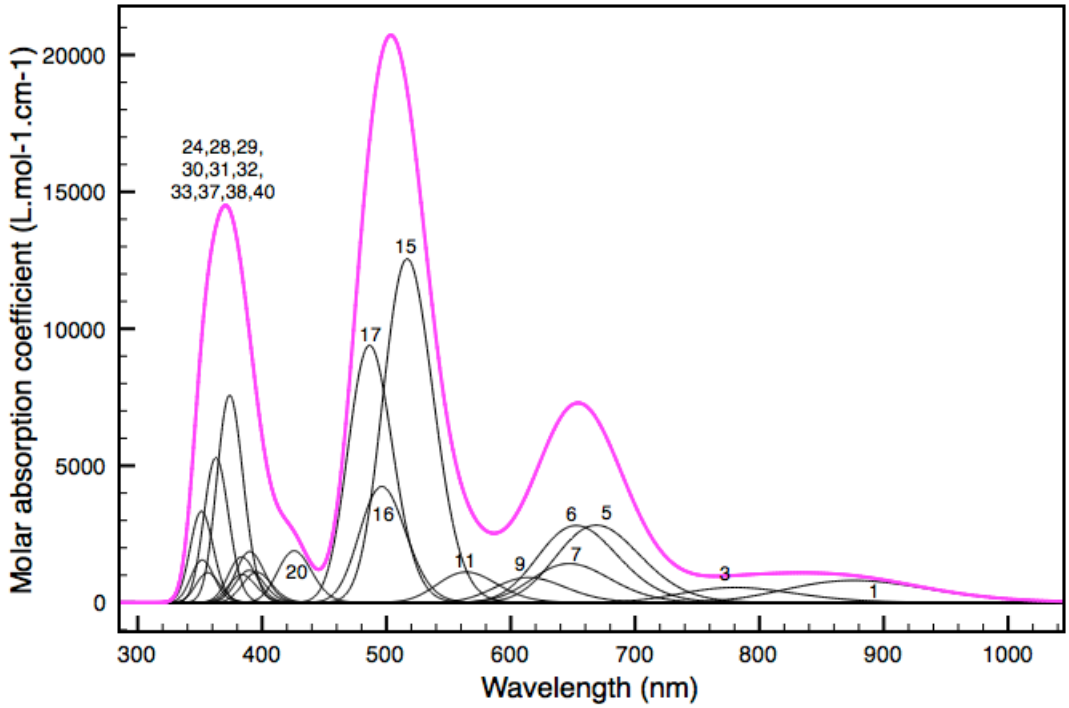


Table S14 : Main transitions found in the absorption spectrum

State	Oscillator strength	Wavelength (nm)	Main components	Major character
1	0.006543395	879.7	133 —> 134 Fe —> L_2	MLCT
3	0.004451988	783.3	132 —> 134 131 —> 135	MLCT

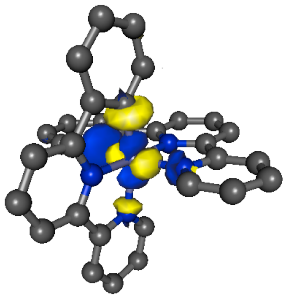
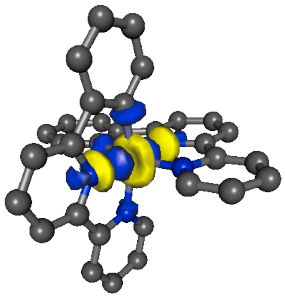
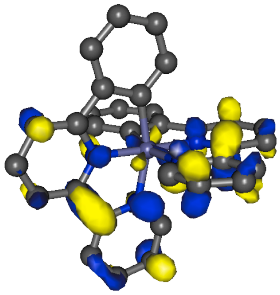
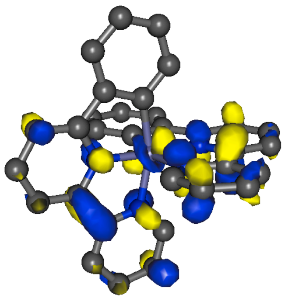
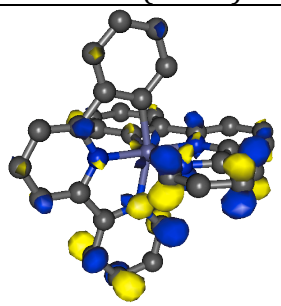
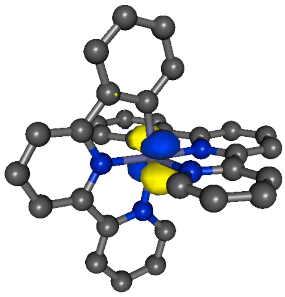
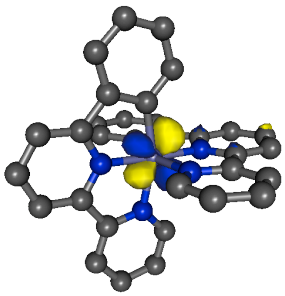
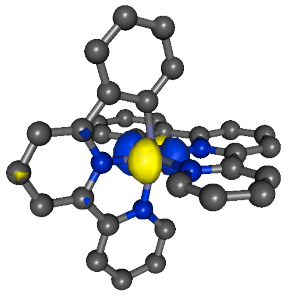
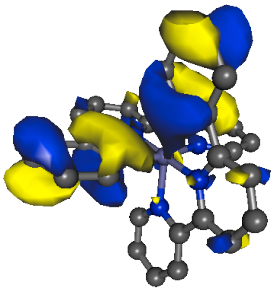
			Fe —> L_2	
5	0.022925342	670.6	133 —> 136 131 —> 135 Fe —> L_2	MLCT
6	0.022818897	654.2	132,133 —> 136 131 —> 135 Fe —> L_2	MLCT
7	0.011532207	648.7	131 —> 136 132 —> 135 Fe —> L_2	MLCT
9	0.007412590	615.7	132 —> 136 131 —> 137 Fe —> L_2	MLCT
11	0.009047740	565.2	131 —> 137 133 —> 138 Fe —> L_2	MLCT
15	0.101920578	517.5	133 —> 138 131 —> 139 Fe —> L_2	MLCT
16	0.034408814	497.0	132 —> 139 131 —> 138 Fe —> L_2	MLCT
17	0.076263215	487.1	131 —> 139 132 —> 138 Fe —> L_2	MLCT
20	0.015306784	426.2	133 —> 139,140 130 —> 136 Fe —> L Fe —> L_2 PhFePh —> L_2	MLCT PBLCT
24	0.0090	396	133 —> 140,141 129 —> 134 128 —> 135 Fe —> L PhFePh —> L_2 CFeC —> L_2	MLCT PBLCT SBLCT
28	0.013530997	383.9	130 —> 137 131 —> 140 PhFePh —> L_2 Fe —> L	PBLCT MLCT
29	0.015090287	390.4	128 —> 135 129 —> 134 CFeC —> L_2 PhFePh —> L_2	SBLCT PBLCT
30	0.009533029	390.0	127 —> 134 CFeC —> L_2	SBLCT
31	0.061389169	374.2	129 —> 135 128 —> 134 133 —> 140	PBLCT SBLCT LC

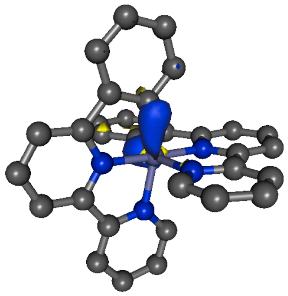
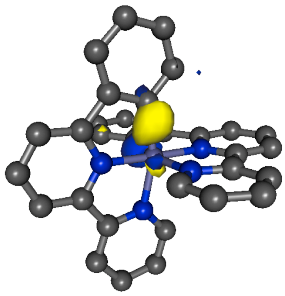
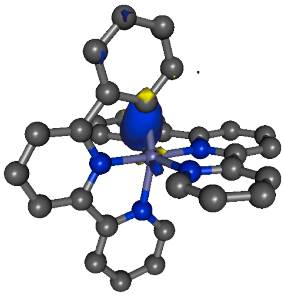
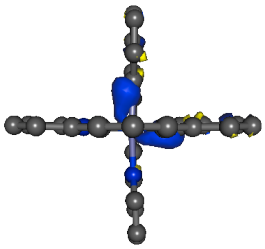
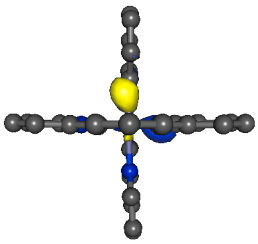
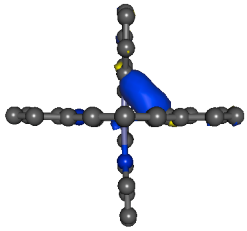
			126 —> 134 PhFePh —> L_2 L_2 —> L_2 Fe —> L	MLCT
33	0.043005278	363.2	132 —> 141 131 —> 140,142 Fe —> L_2 Fe —> FeN_2	MLCT MC
38	0.012602650	352.1	131 —> 142 129 —> 136 Fe —> FeN_2 PhFePh —> L_2	MC PBLCT
40	0.026967033	351.5	128 —> 137 126 —> 135 129 —> 136 PhFePh —> L_2	SBLCT PBLCT
43	0.025535834	344.0	133-144 126-135 Fe —> FeN_2C_2 CFeC —> L_2	MC SBLCT
44	0.031905645	341.1	126-135 133-144 131-143 127-136 CFeC —> L_2 Fe —> FeN_2C_2 Fe —> FeC_2	SBLCT MC
47	0.062136815	334.8	127-136 126-135 131-143 CFeC —> L_2 Fe —> FeC_2	SBLCT MC
50	0.015316471	329.2	128-137 129-138 131-145 133-146 CFeC —> L_2 PhFePh —> L_2 Fe —> FeN_2 Fe —> FeN_2C_2	SBLCT PBLCT MC
51	0.011374973	325.9	131-144 129-137 131-146 Fe —> FeN_2C_2 PhFePh —> L_2	MC PBLCT
53	0.018538416	322.9	133-146 129-138 Fe —> FeN_2C_2 PhFePh —> L_2	MC PBLCT

55	0.019595634	321.0	132-144 129-138 132-146 133-146 Fe —> FeN_2C_2 PhFePh —> L_2	MC PBLCT
62	0.015622011	324.4	128-139 123-134 124-135 CFeC —> L_2 L_2 —> L_2	SBLCT LC
67	0.017260487	304.3	126-137 133-147 127-138 CFeC —> L_2 Fe —> FeN_2C_2	SBLCT MC
68	0.034880881	298.2	133-148 Fe —> L_2	MLCT
69	0.014278686	307.9	132-146 132-147 Fe —> FeN_2C_2	MC
71	0.061724830	296.3	133-149 127-138 Fe —> L_2 CFeC —> L_2	MLCT SBLCT
73	0.025111130	291.8	133-148 126-138 Fe —> L_2 CFeC —> L_2	MLCT SBLCT
75	0.135964848	287.9	133-149 131-148 Fe —> L_2	MLCT
76	0.019056399	286.8	132-148 126-138 124-136 Fe —> L_2 CFeC —> L_2 L_2 —> L_2	MLCT SBLCT LC
77	0.045263531	287.2	132-148 126-138 131-147 Fe —> L_2 CFeC —> L_2 Fe —> FeN_2C_2	MLCT SBLCT MC
78	0.021063853	293.4	132-147 131-148 Fe —> FeN_2C_2 Fe —> L_2	MC MLCT
79	0.010005486	288.7	131-148	MLCT

			132-147 Fe —> L_2 Fe —> FeN_2C_2	MC

Table S15 : Selected B3LYP* orbitals at the PBE0 geometry (eigenvalues in eV)

	 LUMO+11 (+0.95)	 LUMO+12 (+1.02)
 LUMO (-1.96)	 LUMO+1 (-1.83)	 LUMO+2 (-1.47)
 HOMO (-4.15)	 HOMO-1 (-4.45)	 HOMO-2 (-4.45)
 HOMO-3 (-5.17)		

		
HOMO-6 (-5.92)	HOMO-7 (-6.16)	HOMO-8 (-6.61)
		
HOMO-6 sideview	HOMO-7 sideview	HOMO-8 sideview

5. Singlet and triplet excited states at the ground state geometry

Table S16 : TDDFT excited state distribution at the ground state geometries : energy of the states and gaps in eV, and corresponding excited state number.

	1	**2**	**3**	**4**	**5**	**6**	**7**
^{1}MLCT	2.0 (S1)	1.5 (S1)	1.6 (S1)	1.5 (S1)	1.5 (S1)	1.2 (S1)	1.4 (S1)
^{3}MLCT	1.7 (T1)	1.2 (T1)	1.3 (T1)	1.3 (T1)	1.4 (T1)	1.1 (T1)	1.1 (T1)
Gap	0.3	0.3	0.3	0.2	0.1	0.1	0.3
^{1}MC	2.7 (S12)	2.7 (S17)	3.1 (S24)	3.2 (S27)	2.6 (S22)	3.1 (S24)	3.5 (S41)
^{3}MC	2.0 (T7)	2.0 (T8)	2.3 (T13)	2.5 (T18)	2.0 (T15)	2.5 (T20)	3.2 (T36)
Gap	0.7	0.7	0.8	0.7	0.6	0.6	0.3

One can note that the singlet-triplet energy difference is smaller for MLCT states than for MC states, except for complex **7**. In other words, in all cases but **7**, the stabilization occuring upon singlet-to-triplet intersystem crossing is larger in the MC state than in the MLCT state. As a consequence the ^{3}MC-^{3}MLCT gap is smaller than ^{1}MC-^{1}MLCT gap. In the case of **7** however, both states stabilize by the same amount of energy, which should disfavour the MC-MLCT crossing. This is shown schematically below, for complexes **1** (left) and **7** (right).