Supplementary Materials: Controlling the Lifetime of the Triplet MLCT State in Fe(II) Polypyridyl Complexes Through Ligand Modification

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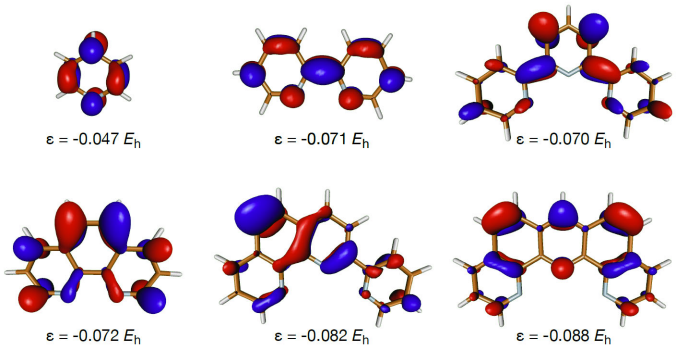

Figure S1. Contour plots of the lowest unoccupied π* orbitals of the ligands used to lower the energy of the MLCT states, iso-surface = 0.05.

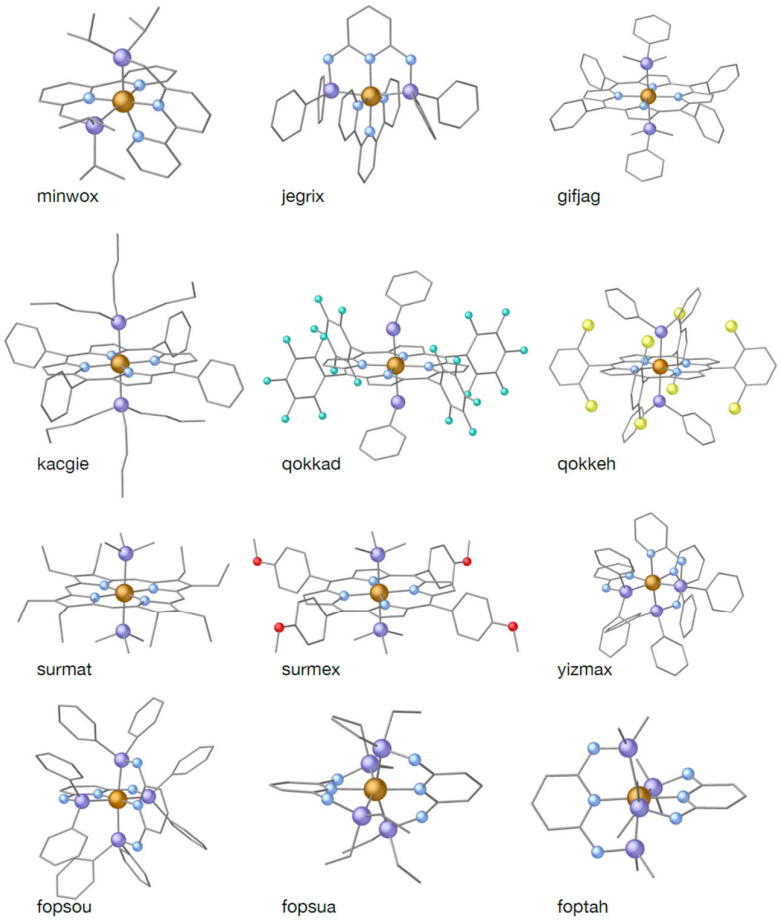

Figure S2. Ball and stick representation of the twelve $FeN_{(6-x)}P_x$ complexes shown in Table 2. Color code: gold = Fe, blue = N, purple = P, light green = F, yellow = Cl, red = O. the grey cylinders represent the carbon skeleton and hydrogens are omitted for clarity.

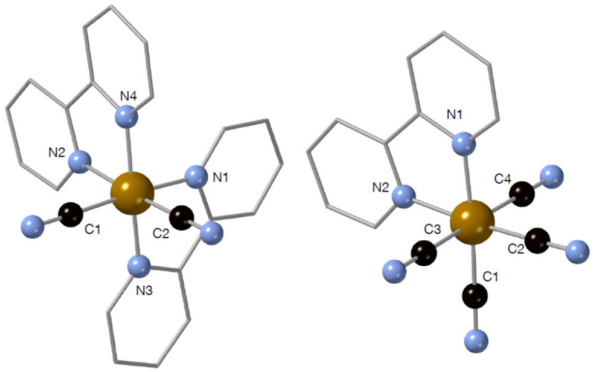

Figure S3. Numbering of the atoms in the first coordination sphere of [Fe(bpy2(CN)2] (left) and $[Fe(bpy)(CN)_4]^{2-}$ (right).

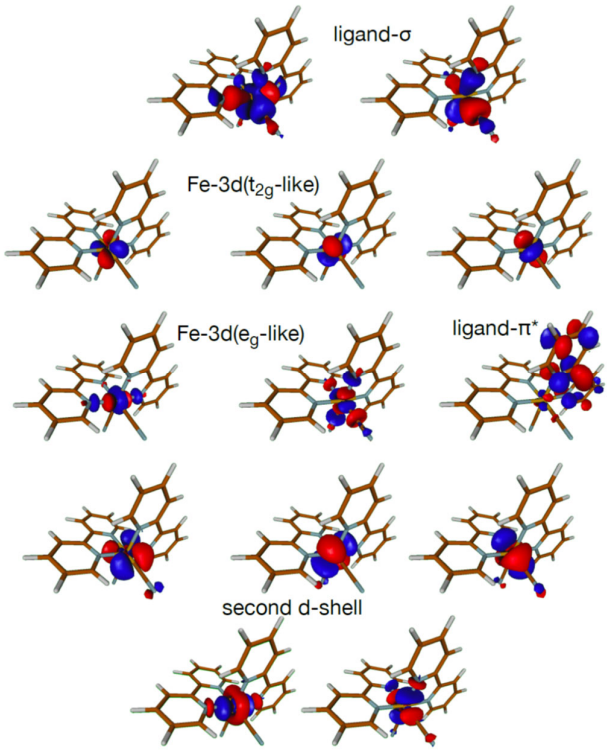

Figure S4. Active orbitals in the CASSCF calculation of the spin-orbit coupling of [Fe(bpy2(CN)2].

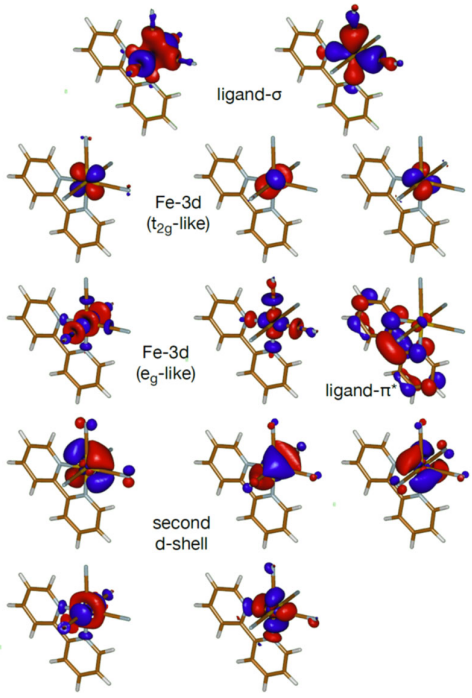

Figure S5. Active orbitals in the CASSCF calculation of the spin-orbit coupling of $[Fe(bpy)(CN)_4]^{2-}$.

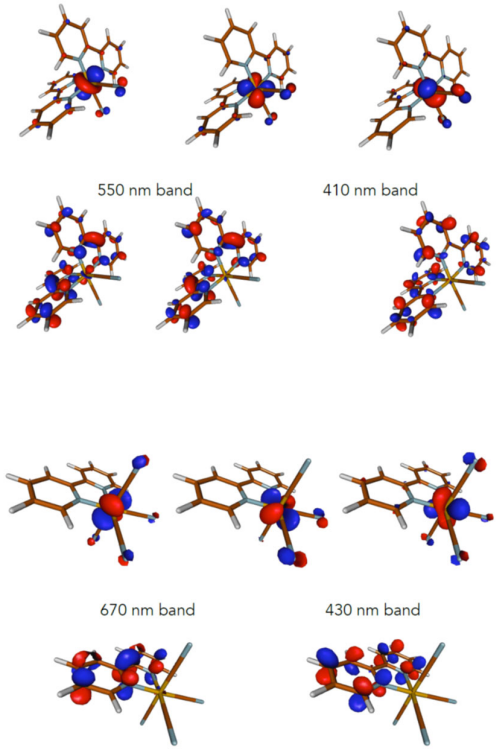

Figure S6. Orbitals involved in the MLCT excitations that give the largest contribution.to the bands in the UV–Vis spectrum of $[Fe(bpy_2(CN)_2]$ (top) and $[Fe(bpy)(CN)_4]^{2-}$ (bottom) calculated with TD-DFT. Excitations involve the three occupied Fe-3d orbitals in row one and three, and the unoccupied π* orbitals in row 2 and 4. The 550 nm band in $Fe(bpy_2(CN)_2$ has contributions from the first two π* orbitals and the largest contribution to the 410 nm shoulder arises from the excitation into the third π* orbital.

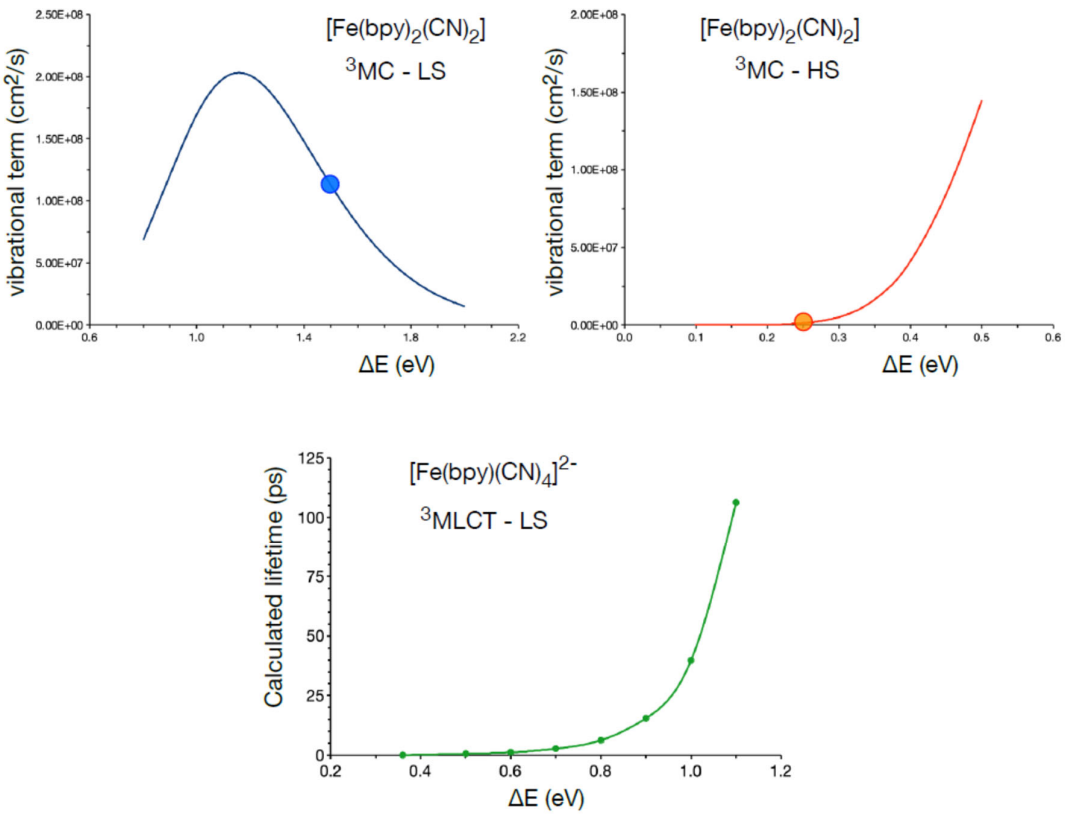

Figure S7. Upper panel: Vibration al contribution to k_{ISC} as function of the adiabatic energy difference for $[Fe(bpy)_2(CN)_2]$. The dot indicates the value at the calculated energy difference. Lower panel: Estimates of the lifetime of the ^{3}MLCT state in $[Fe(bpy)(CN)_4]^{2-}$ as function of the adiabatic energy in the interval between the estimate in gas phase ($\Delta E = 0.48$ eV) and in DMSO ($\Delta E = 1.1$ eV).

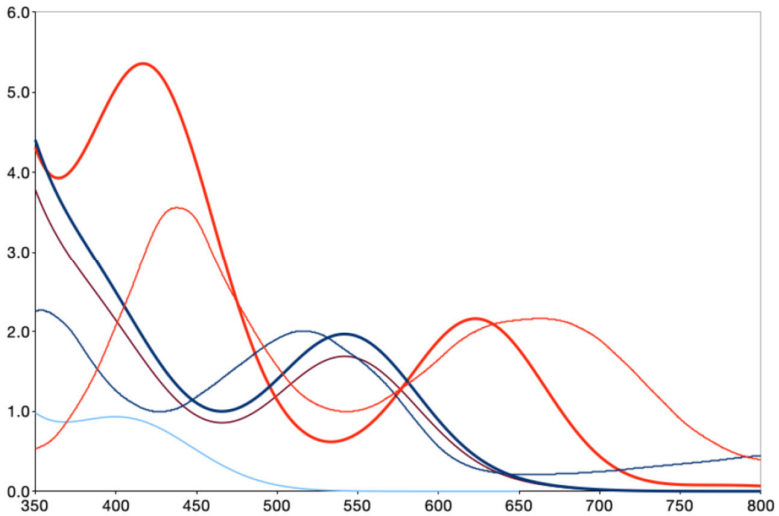

Figure S8. Comparison the calculated UV−Vis spectrum of $[Fe(bpy)_2(CN)_2]$ and $[Fe(bpy)(CN)_4]^{2-}$ to the experimental ones. The thick lines correspond to the TPPSh calculations, the thin blue and red are the experimental spectra and the thin brown and light blue lines are obtained with the CAM-B3LYP functional. The comparison is rather favourable for $[Fe(bpy)_2(CN)_2]$ with both functionals, but CAM-B3LYP completely misses the low-energy peak in the case of $[Fe(bpy)(CN)_4]^{2-}$.

Table S1. Cartesian coordinates [Å] of the TPSSh/def2-TZVP optimised geometry of the LS state of [Fe(bpy2(CN)2].

Atom	*x*	*y*	*z*
Fe	2.990730	0.612299	−3.496994
N	1.931655	0.648260	−5.196953
N	4.681599	0.414575	−4.551209
N	2.866229	2.566626	−3.747785
N	3.162846	−1.353435	−3.451549
C	1.478908	−0.412209	−5.882938
C	1.654535	1.887398	−5.670620
C	0.746525	−0.294644	−7.054086
C	0.921774	2.078573	−6.841018
C	0.461588	0.975225	−7.543784
C	5.077618	−0.864486	−4.763227
C	5.415564	1.405235	−5.080156
C	6.204463	−1.166494	−5.526689
C	6.549215	1.176838	−5.844575
C	6.949238	−0.134498	−6.077888
C	2.183031	2.976332	−4.847962
C	3.375485	3.505274	−2.930122
C	2.010820	4.326768	−5.144870
C	3.240187	4.863862	−3.169758
C	2.546015	5.285976	−4.299034
C	4.228805	−1.867739	−4.118620
C	2.338445	−2.205672	−2.816732
C	4.477423	−3.238454	−4.160142
C	2.528826	−3.578731	−2.822302
C	3.618961	−4.108267	−3.505474
H	1.710672	−1.384775	−5.472718
H	0.407661	−1.187706	−7.562790
H	0.712677	3.078314	−7.196378
H	−0.108511	1.105086	−8.455099
H	5.078689	2.412147	−4.878645
H	6.494273	−2.195824	−5.689346
H	7.099276	2.017468	−6.246959
H	7.826380	−0.350423	−6.674877
H	3.906585	3.134860	−2.064388
H	1.461935	4.622241	−6.028692
H	3.676457	5.570804	−2.476065
H	2.421459	6.339120	−4.518251
H	1.505771	−1.753254	−2.296599
H	5.335173	−3.618111	−4.698463
H	1.829586	−4.213658	−2.293844
H	3.800462	−5.175658	−3.527287
C	3.980483	0.732537	−1.863418
N	4.586723	0.796195	−0.863885
C	1.364573	0.651148	−2.486348
N	0.363391	0.687859	−1.880716

Table S2. Cartesian coordinates [Å] of the TPSSh/def2-TZVP optimised geometry of the ^{3}MC state of [Fe(bpy2(CN)2].

Atom	*x*	*y*	*z*
Fe	2.978941	0.610029	−3.487794
N	1.941201	0.830790	−5.234650
N	4.664710	0.230886	−4.581375
N	2.925858	2.831190	−3.810715
N	3.123508	−1.635273	−3.509760
C	1.539060	−0.220214	−5.966343
C	1.651495	2.078667	−5.676170
C	0.840159	−0.089575	−7.155667
C	0.953506	2.279593	−6.867379
C	0.541461	1.187689	−7.615900
C	5.068798	−1.051371	−4.751888
C	5.365403	1.209500	−5.175385
C	6.173624	−1.361783	−5.545529
C	6.478693	0.970574	−5.964977
C	6.887920	−0.343911	−6.159345
C	2.132586	3.191498	−4.837258
C	3.409847	3.777937	−2.999610
C	1.799116	4.527083	−5.070656
C	3.136952	5.127526	−3.175013
C	2.312424	5.505466	−4.230999
C	4.267474	−2.079511	−4.063118
C	2.334947	−2.500625	−2.863902
C	4.656113	−3.417238	−3.966555
C	2.642557	−3.848532	−2.741258
C	3.830146	−4.311084	−3.299955
H	1.790097	−1.195095	−5.571200
H	0.540980	−0.975156	−7.700864
H	0.741299	3.282814	−7.210028
H	0.001548	1.333114	−8.543234
H	5.010085	2.215935	−5.001894
H	6.465610	−2.393070	−5.689068
H	7.003116	1.802457	−6.416609
H	7.746215	−0.573856	−6.778275
H	4.034814	3.429374	−2.185292
H	1.147318	4.801991	−5.888764
H	3.558059	5.858722	−2.496949
H	2.066285	6.547115	−4.397947
H	1.430110	−2.086901	−2.433538
H	5.590053	−3.756025	−4.394361
H	1.969049	−4.513439	−2.215890
H	4.115460	−5.352458	−3.211869
C	3.961098	0.608165	−1.801424
N	4.563420	0.633378	−0.800017
C	1.347456	0.765874	−2.422676
N	0.355633	0.834730	−1.808155

Table S3. Cartesian coordinates [Å] of the TPSSh/def2-TZVP optimised geometry of the ^{5}MC state of [Fe(bpy2(CN)2].

Atom	*x*	*y*	*z*
Fe	2.923780	0.623914	−3.231958
N	1.857101	0.772962	−5.215655
N	4.752693	0.294884	−4.518587
N	2.816084	2.764667	−3.740524
N	3.188540	−1.555253	−3.423398
C	1.408768	−0.274172	−5.916925
C	1.660755	2.013077	−5.705066
C	0.755550	−0.146781	−7.134558
C	1.013938	2.222572	−6.924930
C	0.558368	1.129957	−7.648054
C	5.084464	−0.984999	−4.779558
C	5.472878	1.272830	−5.078559
C	6.138123	−1.306786	−5.637951
C	6.540176	1.033789	−5.932947
C	6.872119	−0.284656	−6.223243
C	2.165347	3.120983	−4.869021
C	3.281956	3.724351	−2.929168
C	1.979902	4.462987	−5.202989
C	3.130895	5.077049	−3.196316
C	2.467587	5.450782	−4.359658
C	4.264814	−2.009785	−4.100589
C	2.405998	−2.433039	−2.780964
C	4.577264	−3.369317	−4.133095
C	2.651847	−3.798261	−2.776334
C	3.762911	−4.272287	−3.464409
H	1.581861	−1.250378	−5.481564
H	0.413905	−1.028997	−7.660363
H	0.866923	3.222349	−7.308979
H	0.057479	1.275472	−8.597289
H	5.177302	2.284724	−4.830627
H	6.379994	−2.338245	−5.854799
H	7.087743	1.863938	−6.360079
H	7.690020	−0.516174	−6.894339
H	3.796054	3.379233	−2.040431
H	1.455754	4.737583	−6.107740
H	3.528241	5.811327	−2.507889
H	2.328182	6.495369	−4.610276
H	1.555257	−2.011128	−2.259944
H	5.450379	−3.720294	−4.665351
H	1.986749	−4.465125	−2.243349
H	3.997531	−5.329731	−3.480369
C	4.147218	0.915728	−1.497622
N	4.793701	0.982549	−0.527911
C	1.044217	0.466525	−2.216443
N	0.023834	0.462793	−1.649439

Table S4. Cartesian coordinates [Å] of the PBE0/def2-TZVP optimised geometry of the ^{1}MLCT state of [Fe(bpy$_2$(CN)$_2$].

Atom	*x*	*y*	*z*
Fe	3.029827	0.619262	−3.471717
N	2.006582	0.672413	−5.225697
N	4.685790	0.389212	−4.611145
N	2.840725	2.595309	−3.707381
N	3.154868	−1.342561	−3.414238
C	1.616446	−0.389400	−5.922782
C	1.718658	1.901741	−5.675544
C	0.923898	−0.278100	−7.114716
C	1.027565	2.091467	−6.864983
C	0.626131	0.986334	−7.592572
C	5.006531	−0.926166	−4.826071
C	5.440612	1.345433	−5.141650
C	6.116048	−1.242127	−5.640707
C	6.533116	1.099796	−5.941380
C	6.866443	−0.243161	−6.195512
C	2.177606	2.992119	−4.806873
C	3.260302	3.511143	−2.836011
C	1.939918	4.334388	−5.066167
C	3.053260	4.865967	−3.030810
C	2.386179	5.285289	−4.167204
C	4.185488	−1.870878	−4.157809
C	2.386286	−2.161514	−2.687319
C	4.378149	−3.268585	−4.187419
C	2.536392	−3.527120	−2.679027
C	3.562487	−4.090365	−3.462023
H	1.866084	−1.352878	−5.498723
H	0.624527	−1.170620	−7.648184
H	0.799490	3.087675	−7.217863
H	0.084862	1.113199	−8.522529
H	5.151407	2.363556	−4.906492
H	6.373394	−2.277703	−5.819237
H	7.111236	1.919702	−6.343684
H	7.720582	−0.486694	−6.816642
H	3.776716	3.130417	−1.963115
H	1.405440	4.633618	−5.957160
H	3.413449	5.570239	−2.292561
H	2.207583	6.337872	−4.351261
H	1.611209	−1.680150	−2.104660
H	5.186205	−3.684492	−4.774867
H	1.875611	−4.137470	−2.079640
H	3.715332	−5.162941	−3.480497
C	4.117703	0.791658	−1.960423
N	4.825515	0.987370	−1.059917
C	1.400438	0.698196	−2.511724
N	0.368114	0.736530	−1.983318

Table S5. Selected distances (in Å) and angles (in degrees) of the FeN_4C_2-core of $[Fe(bpy_2(CN)_2]$. Atom labels follow the numbering in Figure S1.

	LS	^{3}MC	^{5}MC	^{1}MLCT
Fe–N1	2.002	2.045	2.260	2.023
Fe–N2	2.003	2.044	2.257	2.032
Fe–N3	1.974	2.250	2.203	1.999
Fe–N4	1.974	2.245	2.204	1.967
Fe–C1	1.915	1.955	2.142	1.893
Fe–C2	1.914	1.952	2.142	1.870
C1–Fe–C2	89.3	87.1	97.3	95.0
N1–Fe–N3	80.8	75.9	73.1	81.4
N2–Fe–N4	80.9	76.0	73.1	79.9
C1–Fe–N1	175.5	173.9	165.7	174.2
C2–Fe–N2	175.3	173.8	166.5	171.3

Table S6. Cartesian coordinates [Å] of the TPSSh/def2-TZVP optimised geometry of the LS state of $[Fe(bpy)(CN)_4]^{2-}$.

Atom	*x*	*y*	*z*
Fe	2.950203	0.661915	−3.495418
N	1.925635	0.727134	−5.209723
N	2.811702	2.640430	−3.726934
C	1.509982	−0.330067	−5.926324
C	1.629777	1.968875	−5.667333
C	0.790215	−0.204870	−7.104275
C	0.906257	2.166140	−6.843969
C	0.478183	1.067729	−7.573225
C	2.138960	3.054930	−4.829339
C	3.317993	3.574230	−2.904573
C	1.966190	4.408125	−5.120351
C	3.182430	4.934462	−3.134579
C	2.492490	5.363366	−4.265091
H	1.774033	−1.299211	−5.525290
H	0.481297	−1.095105	−7.637222
H	0.681026	3.168305	−7.183182
H	−0.084698	1.202136	−8.488619
H	3.846373	3.197219	−2.039319
H	1.424409	4.708273	−6.007309
H	3.614465	5.638341	−2.434675
H	2.366577	6.417916	−4.477900
C	3.921536	0.765770	−1.862628
N	4.519798	0.834725	−0.855400
C	1.296057	0.635215	−2.490725
N	0.290242	0.620819	−1.888802
C	2.999081	−1.236224	−3.410874
N	3.026605	−2.408607	−3.361510
C	4.621564	0.638274	−4.468957
N	5.631550	0.628251	−5.064001

Table S7. Cartesian coordinates [Å] of the TPSSh/def2-TZVP optimised geometry of the ^{3}MLCT state of $[Fe(bpy)(CN)_4]^{2-}$.

Atom	*x*	*y*	*z*
Fe	2.945443	0.675383	−3.511398
N	1.934628	0.718884	−5.220375
N	2.822351	2.645880	−3.725356
C	1.531062	−0.341026	−5.941763
C	1.630624	2.000747	−5.665581
C	0.809416	−0.231891	−7.111986
C	0.883029	2.161902	−6.861721
C	0.474684	1.065786	−7.575824
C	2.123676	3.048988	−4.858417
C	3.323737	3.578081	−2.896709
C	1.958528	4.434769	−5.116642
C	3.188247	4.934300	−3.108225
C	2.480325	5.367280	−4.259027
H	1.808737	−1.309288	−5.544683
H	0.509895	−1.123450	−7.646766
H	0.636895	3.159923	−7.202666
H	−0.097353	1.191499	−8.487924
H	3.854053	3.197962	−2.032593
H	1.414371	4.746909	−5.999565
H	3.617531	5.635568	−2.405048
H	2.351566	6.424476	−4.461617
C	3.921053	0.702408	−1.847826
N	4.513509	0.720543	−0.842771
C	1.265663	0.710015	−2.490873
N	0.264638	0.737776	−1.893748
C	3.023637	−1.245886	−3.362873
N	3.064599	−2.408878	−3.276345
C	4.628820	0.633080	−4.523086
N	5.626570	0.616758	−5.126139

Table S8. Selected distances (in Å) and angles (in degrees) of the FeN_2C_4-core of $[Fe(bpy)(CN)_4]^{2-}$. Atom labels follow the numbering in Figure S1.

	LS	**^{3}MLCT**
Fe–N1	1.998	1.986
Fe–N2	1.997	1.986
Fe–C1	1.901	1.929
Fe–C2	1.903	1.929
Fe–C3	1.936	1.966
Fe–C4	1.934	1.964
C1–Fe–C2	90.2	85.8
C3–Fe–C4	178.2	179.6
N1–Fe–N2	80.4	81.6
C1–Fe–N1	175.2	177.3
C2–Fe–N2	175.0	177.9

Table S9. Selected optimised distances (in Å) of the ^{1}MLCT state of $[Fe(bpy)(CN)_4]^{2-}$ in gas phase and in DMSO (modelled with C-PCM). Atom labels follow the numbering in Figure S1.

	Gas Phase	DMSO	Δr
Fe–N1	2.032	1.991	0.041
Fe–N2	2.035	1.991	0.044
Fe–C1	1.906	1.910	0.004
Fe–C2	1.908	1.910	0.002
Fe–C3	1.945	1.940	0.005
Fe–C4	1.945	1.939	0.006