Supplementary Information

Halogenation Affects Driving Forces, Reorganization Energies and "Rocking" Motions in Strained $[Fe(tpy)_2]^{2+}$ Complexes

*Hyuk-Yong Kwon, Daniel C. Ashley, Elena Jakubikova**

Department of Chemistry, North Carolina State University, Raleigh, North Carolina 27695, United States

Table of Contents

Table S1. Electronic energies (E), zero-point energies (ZPE), entropic corrections to free energies (−TS), enthalpies (H), and solvated Gibbs free energies (G) calculated with DFT. All optimizations were done with the IEFPCM correction for solvent (water), hence E contains the effects of solvation already. The temperature (T) was taken as 298.15 K, and the pressure as 1 atm. All values are reported in kcal/mol.

Complex	E	ZPE	−TS	H	G
Heptet H	-1009730.1	286.2	-57.3	-1009425.3	-1009482.6
Quintet H	-1009773.8	288.1	-57.9	-1009467.1	-1009525.0
Triplet H	-1009764.2	288.4	-56.6	-1009457.4	-1009513.9
Singlet H	-1009779.4	289.8	-53.1	-1009471.9	-1009525.0
Heptet F	-1258900.6	265.2	-62.6	-1258614.6	-1258677.1
Quintet F	-1258951.1	267.0	-63.4	-1258663.2	-1258726.6
Triplet F	-1258939.3	267.7	-61.6	-1258651.1	-1258712.7
Singlet F	-1258948.3	268.9	-58.0	-1258659.5	-1258717.5
Heptet Cl	-2163385.7	261.6	-63.6	-2163102.5	-2163166.1
Quintet Cl	-2163439.4	263.5	-64.7	-2163154.2	-2163218.9
Triplet Cl	-2163426.1	264.0	-64.6	-2163140.6	-2163205.2
Singlet Cl	-2163428.9	264.7	-61.7	-2163143.1	-2163204.8
Heptet Br	-7469405.9	259.8	-65.9	-7469123.8	-7469189.7
Quintet Br	-7469460.2	261.4	-68.2	-7469176.2	-7469244.4
Triplet Br	-7469446.2	262.1	-66.7	-7469161.8	-7469228.6
Singlet Br	-7469448.1	262.8	-64.1	-7469163.5	-7469227.6
Heptet I	-1036841.9	258.4	-67.9	-1036560.7	-1036628.6
Quintet I	-1036897.3	260.4	-68.8	-1036613.9	-1036682.7
Triplet I	-1036882.8	260.7	-68.8	-1036599.4	-1036668.2
Singlet I	-1036884.0	261.4	-66.0	-1036600.2	-1036666.2

Table S2. Electronic single point energies taken at alternative spin states. Each column labelled SPX contains single point energy calculations performed with "X" spin state at the optimized geometry of the given complex/spin state. When X is H, Q, or T it refers to heptet, quintet, or triplet respectively. All SPX energies are taken at the same level of theory as "E" in Table S1. All values are reported in kcal/mol.

Complex	SPH	SPQ	SPT
Heptet H	-1009730.1	-1009766.0	-1009754.4
Quintet H	-1009721.4	-1009773.8	-1009748.7
Triplet H	-1009721.3	-1009761.9	-1009764.2
Heptet F	-1258900.6	-1258943.0	-1258931.1
Quintet F	-1258892.0	-1258951.1	-1258928.9
Triplet F	-1258892.7	-1258939.6	-1258939.3
Heptet Cl	-2163385.7	-2163431.2	-2163414.4
Quintet Cl	-2163377.5	-2163439.4	-2163416.8
Triplet Cl	-2163379.3	-2163429.2	-2163426.1
Heptet Br	-7469405.9	-7469452.2	-7469433.5
Quintet Br	-7469398.0	-7469460.2	-7469435.4
Triplet Br	-7469399.4	-7469449.5	-7469446.2
Heptet I	-1036841.9	-1036889.5	-1036869.0
Quintet I	-1036834.1	-1036897.3	-1036871.4
Triplet I	-1036835.7	-1036886.4	-1036882.8

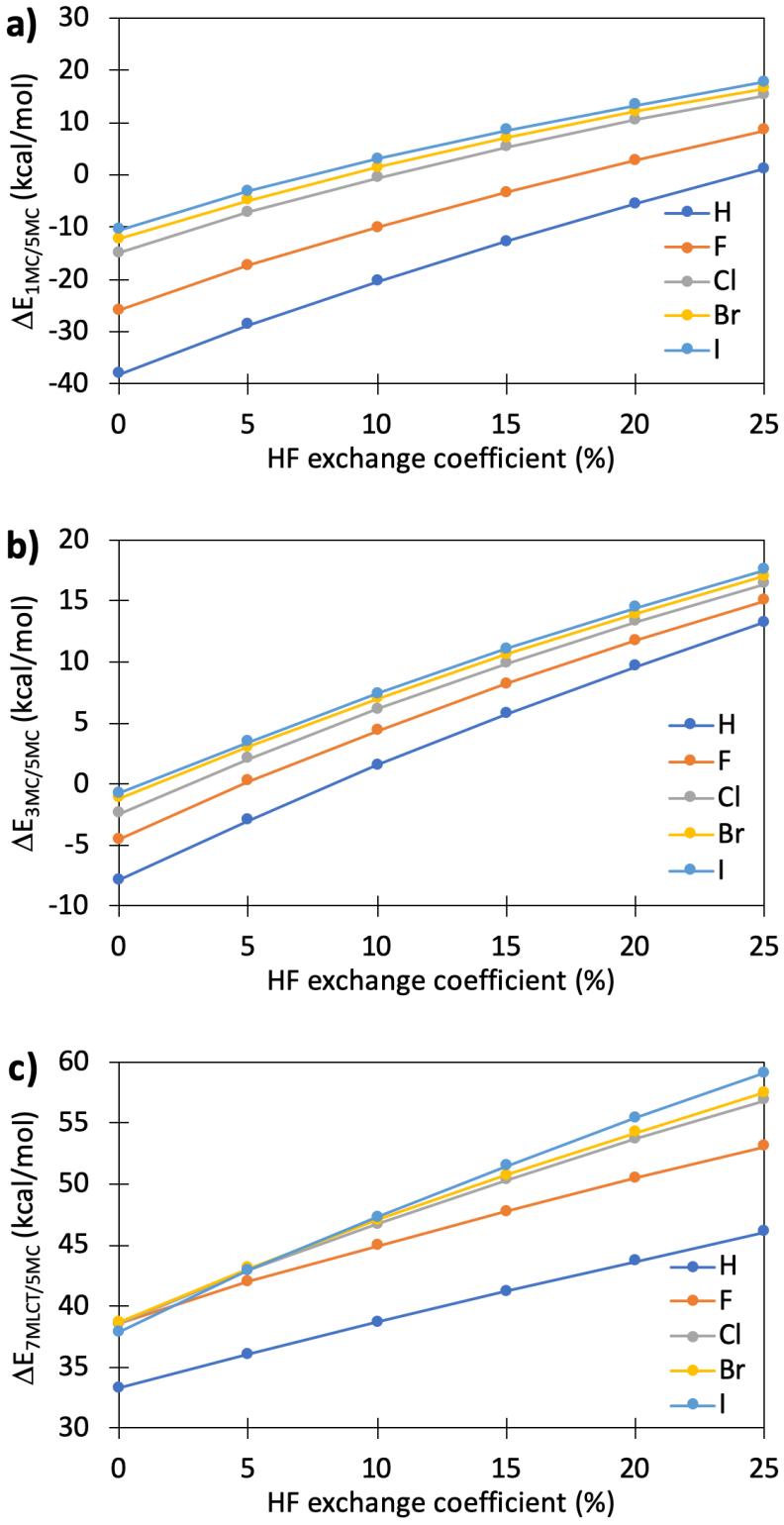

Figure S1. The spin-state energy difference for ^{1}MC (a), ^{3}MC (b) and ^{7}MLCT (c) relative to ^{5}MC versus exact exchange in B3LYP functional for $[Fe(tpy^{X})_2]^{2+}$.