

Supporting Information

Ultrafast Intersystem Crossing vs. Internal Conversion in α -diimine Transition Metal Complexes: Quantum Evidence

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The diabatic Hamiltonian describing n_{el} coupled electronic states is written as

$$\mathbf{H}(\mathbf{Q}) = (T_N + V_0(\mathbf{Q}))\mathbb{I} + \mathbf{W}(\mathbf{Q}) \quad (1)$$

where T_N is the kinetic energy operator, $V_0(\mathbf{Q})$ is the potential energy of the reference electronic state, $\mathbb{I}$ is the $n_{el} \times n_{el}$ identity matrix and $\mathbf{W}(\mathbf{Q})$ the coupling matrix. $\mathbf{Q}$ collects the nuclear degrees of freedom. The adiabatic potential energy surfaces $V_n(\mathbf{Q})$ are provided as the eigenvalues of $V_0(\mathbf{Q})\mathbb{I} + \mathbf{W}(\mathbf{Q})$.

The reference potential V_0 is described using the harmonic approximation for the electronic ground state, written in terms of mass- and frequency-weighted (dimensionless) normal coordinates Q_i .¹

$$T_N + V_0(\mathbf{Q}) = \sum_i \frac{\omega_i}{2} \left(-\frac{\partial^2}{\partial Q_i^2} + Q_i^2 \right) \quad (2)$$

with ω_i the harmonic frequency of mode i . The elements of the coupling matrix $\mathbf{W}(\mathbf{Q})$ represent the changes in the excited state potentials with respect to $V_0(\mathbf{Q})$ and vary smoothly

¹ (a) H. Köppel, W. Domcke, and L. S. Cederbaum, Adv. Chem. Phys. **57**, 59-246 (1984). (b) H. Köppel, and W. Domcke, in *Encyclopedia in Computational Chemistry*, edited by P. von Ragué Schleyer (Wiley, New York, 1998), pp. 3166. (c) G. A. Worth, and L. S. Cederbaum, Annu. Rev. Phys. Chem. **55**, 127 (2004).

as a function of nuclear displacements. They are expanded in Taylor series around the reference geometry (here taken to be the Franck-Condon point, $\mathbf{Q}=\mathbf{0}$):

$$W_{nn}(\mathbf{Q}) = \varepsilon_n + \sum_i \kappa_i^{(n)} Q_i + \frac{1}{2} \sum_{i,j} \gamma_{ij}^{(n)} Q_i Q_j + \dots \quad (3)$$

$$W_{nm}(\mathbf{Q}) = \sum_i \lambda_i^{(nm)} Q_i + \dots \quad n \neq m \quad (4)$$

where in Eq. (3) ε_n is the vertical excitation energy for state n , $\kappa_i^{(n)}$ is the first-order (linear) intrastate coupling constant along mode i for state n , $\gamma_{ij}^{(n)}$ the bilinear intrastate coupling constant for mode i and j for state n , etc. In Eq. (4), $\lambda_i^{(nm)}$ corresponds to the linear interstate coupling between states n and m , for $n \neq m$.

The symmetry selection rules strongly restrict the number of nonzero electronic-vibrational coupling constants, which largely simplifies the problem of parametrizing these constants. For the linear terms within a two-state problem, one gets.¹

$$\Gamma_n \otimes \Gamma_Q \otimes \Gamma_m \supset \Gamma_A \quad (5)$$

where Γ_n and Γ_m refer to the electronic state symmetry, Γ_Q to the normal mode symmetry and Γ_A is the totally symmetric irreducible representation of the symmetry point group of the molecule.

The determination of $\kappa_i^{(n)}$ is relatively straightforward from the calculation of the gradients at Franck-Condon, provided analytically,

$$\kappa_i^{(n)} = \left. \frac{\partial V_n(\mathbf{Q})}{\partial Q_i} \right|_0 \quad (6)$$

$\lambda_i^{(nm)}$ coupling term which measures the repulsion between states n and m along the mode i , has been obtained at the time-dependent density functional theory level through the overlap

integrals between excited-state adiabatic auxiliary wavefunctions (Ref. 26)

$$\lambda_i^{(nm)} = \left. \frac{\partial W_{nm}(\mathbf{Q})}{\partial Q_i} \right|_0 = \left. \frac{\partial}{\partial Q_i} \langle \Phi_n | H_{el} | \Phi_m \rangle \right|_0$$

where Φ_n and Φ_m are the diabatic wavefunctions and H_{el} the (spin-free) electronic Hamiltonian.

The effective vibronic coupling constants presented in Table 1 and Tables S2-S5 are defined as the square root of the sum of the squares of the coupling constants summed over some selected modes. Note that the three triplet's components are explicitly considered in the $n_{el} \times n_{el} \mathbf{W}(\mathbf{Q})$ the coupling matrix. In addition to the vibronic coupling terms, $\mathbf{W}(\mathbf{Q})$ also contains spin-orbit coupling, here taken to be constant at their Franck-Condon values.

Electronic structure calculations of $[\text{Mn}(\text{im})(\text{CO})_3(\text{phen})]^+$ and $[\text{Re}(\text{im})(\text{CO})_3(\text{phen})]^+$ were performed under Cs symmetry by means of density functional theory (DFT)² including water solvent corrections based on a conductor-like screening model (COSMO).³

The calculations were performed using the B3LYP functional⁴ and all electron triple-z basis set.⁵ The scalar relativistic effects were taken into account within the zeroth-order regular approximation (ZORA).⁶ The vertical transition energies were computed within TD-DFT⁷ at the same level described above under the Tamm-Dancoff approximation (TDA).⁸ The non-equilibrium solvation within the linear-response TDDFT with a high-frequency dielectric

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³ (a) A. Klamt, A., G. J. Schuurmann, Chem. Soc., Perkin Trans. 2 1993, 2, 799. (b) A. Klamt, J. Phys. Chem. 1995, 99, 2224. (c) A. Klamt, A., V. Jonas, J. Chem. Phys. 1996, 105, 9972.

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⁵ E. Van Lenthe, E. J. Baerends, J. Comput. Chem. 2003, 24, 1142.

⁶ E. Van Lenthe, R. Van Leeuwen, E. J. Baerends, J. G. Snijders, Int. J. Quantum Chem. 1996, 57, 281.

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vt9 = 0.1790 eV = 1444 cm⁻¹
vt10 = 0.1926 eV = 1554 cm⁻¹
vt11 = 0.2013 eV = 1623 cm⁻¹
vt12 = 0.2058 eV = 1660 cm⁻¹
vc1 = 0.0112 eV = 90 cm⁻¹
vc2 = 0.0589 eV = 476 cm⁻¹
vc3 = 0.0783 eV = 631 cm⁻¹

[illegible]

vt1 = 0.0221 eV = 178 cm⁻¹
vt2 = 0.0242 eV = 195 cm⁻¹
vt3 = 0.0268 eV = 216 cm⁻¹
vt4 = 0.0315 eV = 254 cm⁻¹
vt5 = 0.1924 eV = 1552 cm⁻¹
vt6 = 0.0801 eV = 646 cm⁻¹
vt7 = 0.0857 eV = 691 cm⁻¹
vt8 = 0.0928 eV = 749 cm⁻¹

wt9 = 0.0570 eV = 460 cm⁻¹
wt10 = 0.0584 eV = 471 cm⁻¹
wt11 = 0.2014 eV = 1625 cm⁻¹
wt12 = 0.2059 eV = 1661 cm⁻¹
wc1 = 0.0119 eV = 96 cm⁻¹
wc2 = 0.0590 eV = 475 cm⁻¹
wc3 = 0.0790 eV = 637 cm⁻¹

¹³ M. Fumanal, E. Gindensperger, C. Daniel, J. Chem. Theory Comput. 13, 1293(2017)

(a) $[\text{Re}(\text{CO})_3(\text{phen})(\text{im})]^+$			(b) $[\text{Mn}(\text{CO})_3(\text{phen})(\text{im})]^+$		
LUMO+4	LUMO+3	LUMO+2	LUMO+4	LUMO+3	LUMO+2
81a' -0.0295	47a'' -0.0414	80a' -0.0438	65a' -0.0298	38a'' -0.0384	64a' -0.0402
LUMO+1	LUMO		LUMO+1	LUMO	
46a'' -0.0850	79a' -0.0956		37a'' -0.0813	63a' -0.0889	
HOMO	HOMO-1	HOMO-2	HOMO	HOMO-1	HOMO-2
45a'' -0.2377	78a' -0.2449	77a' -0.2517	36a'' -0.2376	62a' -0.2437	61a' -0.2499
HOMO-3	HOMO-4	HOMO-5	HOMO-3	HOMO-4	HOMO-5
44a'' -0.2582	76a' -0.2665	43a'' -0.2761	35a'' -0.2543	60a' -0.2621	34a'' -0.2721

Figure S1. Kohn-Sham frontier orbitals of $[\text{Re}(\text{im})(\text{CO})_3(\text{phen})]^+$ (left) and $[\text{Mn}(\text{im})(\text{CO})_3(\text{phen})]^+$ (right) in COSMO water in the S_0 electronic ground state.

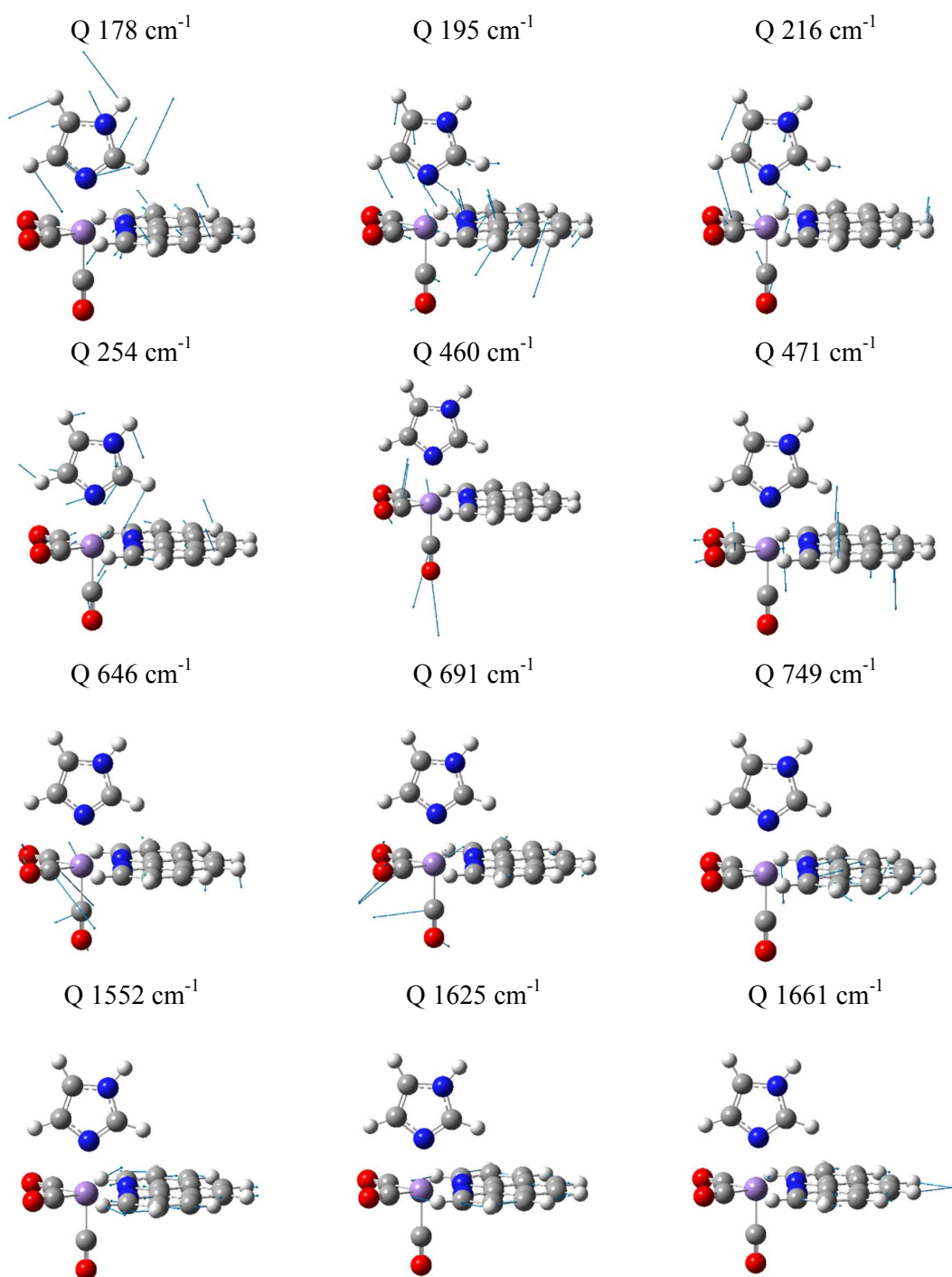


Figure S2. Nuclear deformation associated with the most relevant a' modes of $\text{Mn}(\text{CO})_3(\text{im})(\text{phen})^+$ selected for the dynamics simulations.

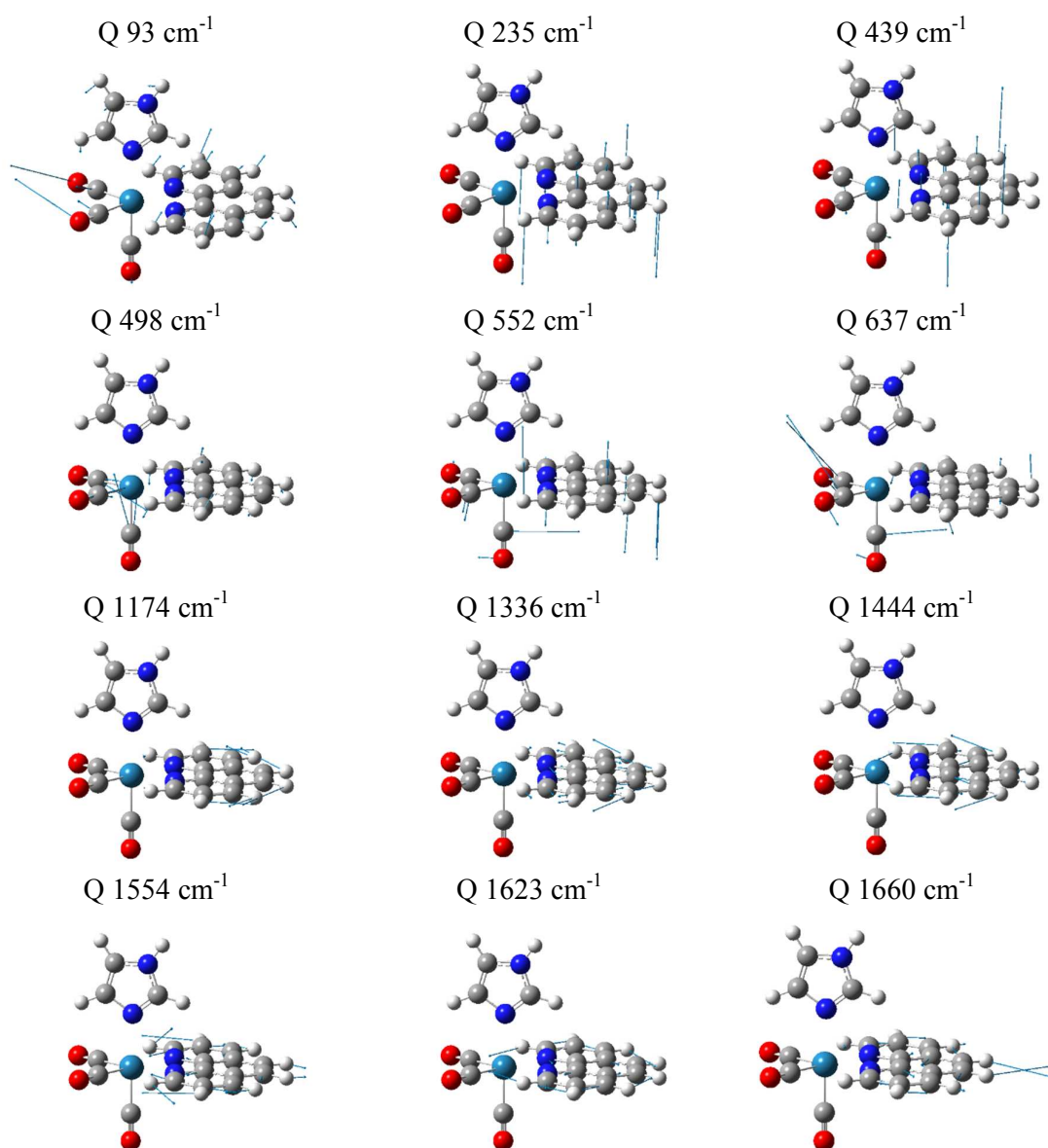


Figure S3. Nuclear deformation associated with the most relevant a' modes of $\text{Re}(\text{CO})_3(\text{im})(\text{phen})^+$ selected for the dynamics simulations.

Table S1. TD-DFT/TDA transition energies (in eV), wavelengths of absorption (in nm) and oscillator strengths f associated to the low-lying excited states of $\text{Re}(\text{CO})_3(\text{phen})(\text{imi})^+$ (left) and $\text{Mn}(\text{CO})_3(\text{phen})(\text{imi})^+$ (right). The main one-electron excitations are indicated following the orbital notation depicted in Fig S1.

$\text{Re}(\text{CO})_3(\text{phen})(\text{imi})^+$						$\text{Mn}(\text{CO})_3(\text{phen})(\text{imi})^+$					
State		One-electron excitation	Trans. E	Wave length	f	State		One-electron excitation	Trans. E	Wave length	f
T ₁	A ³ A"	83% 45a"-79a'	2.98	416		T ₁	A ³ A'	77% 36a"-38a"	2.92	425	
T ₂	A ³ A'	84% 78a'-79a'	3.07	403		T ₂	A ³ A"	46% 36a"-63a' 25% 36a"-65a'	2.95	420	
S ₁	a ¹ A"	99% 45a"-79a'	3.12	398	0.002	T ₃	B ³ A'	54% 62a'-63a' 20% 62a'-65a'	3.09	401	
T ₃	B ³ A"	47% 78a'-46a" 32% 76a'-46a"	3.24	382		T ₄	B ³ A"	54% 61a'-38a" 23% 62a'-38a"	3.10	400	
S ₂	b ¹ A'	66% 78a'-79a' 22% 45a"-46a" 11% 77a'-79a'	3.40	365	0.054	T ₅	C ³ A"	17% 62a'-37a" 17% 60a'-37a" 12% 36a"-65a' 12% 62a'-38a" 12% 36a"-63a'	3.17	391	
T ₄	B ³ A'	82% 77a'-79a'	3.42	363		S ₁	a ¹ A"	91% 36a"-63a'	3.19	389	0.001
T ₅	C ³ A'	82% 45a"-46a"	3.45	359		T ₆	D ³ A"	33% 62a'-38a" 17% 61a'-38a"	3.22	385	
S ₃	c ¹ A'	80% 77a'-79a'	3.46	358	0.003	T ₇	C ³ A'	19% 61a'-65a' 19% 61a'-63a' 17% 62a'-65a' 16% 62a'-63a'	3.23	384	
T ₆	C ³ A"	73% 43a"-79a'	3.56	348		T ₈	E ³ A"	36% 36a"-63a' 19% 62a'-37a" 16% 36a"-65a' 16% 60a'-37a"	3.32	373	
S ₄	d ¹ A'	59% 45a"-46a" 30% 78a'-79a'	3.56	349	0.117	T ₉	D ³ A'	19% 61a'-65a' 17% 62a'-65a' 16% 61a'-63a' 10% 60a'-63a'	3.34	371	
T ₇	D ³ A'	84% 76a'-79a'	3.57	347		S ₂	b ¹ A'	73% 62a'-63a' 11% 36a"-37a"	3.43	362	0.053
S ₅	b ¹ A"	86% 78a'-46a"	3.76	329	0.024	T ₁₀	E ³ A'	41% 36a"-37a" 16% 60a'-63a' 10% 61a'-63a'	3.48	356	
T ₈	D ³ A"	27% 78a'-46a" 28% 76a'-46a" 33% 77a'-46a"	3.82	325		S ₃	c ¹ A'	80% 61a'-63a' 14% 36a"-37a"	3.52	352	0.003
S ₆	c ¹ A"	98% 44a"-79a'	3.83	324	0.002	T ₁₁	F ³ A'	52% 36a"-37a" 16% 60a'-63a' 12% 61a'-63a'	3.54	350	
T ₉	E ³ A"	71% 44a"-79a' 16% 43a"-79a'	3.84	323		S ₄	b ¹ A"	31% 36a"-65a' 29% 62a'-38a"	3.56	348	0.000
T ₁₀	E ³ A'	67% 43a"-46a"	3.90	320		S ₅	d ¹ A'	72% 36a"-37a" 10% 62a'-63a'	3.59	346	0.060

Table S2. Effective vibronic coupling (in eV) between the singlet S1-S6 excited states of [Re(imidazole)(CO)₃(phen)]⁺ associated to the a' CO modes (93, 498, 552, 637 cm⁻¹), a' phen modes (235, 439, 1174, 1336, 1444, 1554, 1623, 1660 cm⁻¹) and a'' CO modes (90, 475, 631 cm⁻¹). Diagonal terms correspond to intrastate kappa obtained by means of the gradient computed at FC and off-diagonal terms correspond to interstate coupling lambda obtained within the overlap protocol of Ref 26.

a' (CO)	S1 A''	S2 A'	S3 A'	S4 A'	S5 A''	S6 A''
S1 A''	0.0372					
S2 A'	0.0	0.0420				
S3 A'	0.0	0.0073	0.0305			
S4 A'	0.0	0.0156	0.0021	0.0148		
S5 A''	0.0029	0.0	0.0	0.0	0.0708	
S6 A''	0.0107	0.0	0.0	0.0	0.0074	0.0225
a' (phen)	S1 A''	S2 A'	S3 A'	S4 A'	S5 A''	S6 A''
S1 A''	0.2825					
S2 A'	0.0	0.2064				
S3 A'	0.0	0.0587	0.2167			
S4 A'	0.0	0.1035	0.0950	0.1653		
S5 A''	0.0203	0.0	0.0	0.0	0.2297	
S6 A''	0.0165	0.0	0.0	0.0	0.0361	0.2599
a'' (CO)	S1 A''	S2 A'	S3 A'	S4 A'	S5 A''	S6 A''
S1 A''	0.0041					
S2 A'	0.0216	0.0033				
S3 A'	0.0344	0.0	0.0040			
S4 A'	0.0292	0.0	0.0	0.0043		
S5 A''	0.0	0.0062	0.0161	0.0318	0.0036	
S6 A''	0.0	0.0067	0.0057	0.0042	0.0	0.0008

Table S3. Effective vibronic coupling (in eV) between the triplet T1-T8 excited states of [Re(imidazole)(CO)₃(phen)]⁺ associated to the a' CO modes (93, 498, 552, 637 cm⁻¹), a' phen modes (235, 439, 1174, 1336, 1444, 1554, 1623, 1660 cm⁻¹) and a'' CO modes (90, 475, 631 cm⁻¹). Diagonal terms correspond to intrastate kappa obtained by means of the gradient computed at FC and off-diagonal terms correspond to interstate coupling lambda obtained within the overlap protocol of Ref. 26.

a' (CO)	T1 A''	T2 A'	T3 A''	T4 A'	T5 A'	T6 A''	T7 A'	T8 A''
T1 A''	0.0294							
T2 A'	0.0	0.0351						
T3 A''	0.0253	0.0	0.0096					
T4 A'	0.0	0.0306	0.0	0.0031				
T5 A'	0.0	0.0083	0.0	0.0054	0.0321			
T6 A''	0.0146	0.0	0.0077	0.0	0.0	0.0073		
T7 A'	0.0	0.0418	0.0	0.0297	0.0050	0.0	0.0037	
T8 A''	0.0129	0.0	0.0314	0.0	0.0	0.0151	0.0	0.0552
a' (phen)	T1 A''	T2 A'	T3 A''	T4 A'	T5 A'	T6 A''	T7 A'	T8 A''
T1 A''	0.2637							
T2 A'	0.0	0.2820						
T3 A''	0.1172	0.0	0.3597					
T4 A'	0.0	0.0341	0.0	0.2325				
T5 A'	0.0	0.0466	0.0	0.0773	0.2057			
T6 A''	0.0864	0.0	0.0898	0.0	0.0	0.2941		
T7 A'	0.0	0.0817	0.0	0.0192	0.0524	0.0	0.2389	
T8 A''	0.0275	0.0	0.0702	0.0	0.0	0.0253	0.0	0.2329
a'' (CO)	T1 A''	T2 A'	T3 A''	T4 A'	T5 A'	T6 A''	T7 A'	T8 A''
T1 A''	0.0							
T2 A'	0.0367	0.0						
T3 A''	0.0	0.0062	0.0					
T4 A'	0.0340	0.0	0.0122	0.0				
T5 A'	0.0195	0.0	0.0120	0.0	0.0			
T6 A''	0.0	0.0041	0.0	0.0033	0.0093	0.0		
T7 A'	0.0197	0.0	0.0051	0.0	0.0	0.0098	0.0	
T8 A''	0.0	0.0157	0.0	0.0102	0.0309	0.0	0.0149	0.0

Table S4. Effective vibronic coupling (in eV) between the singlet S1-S9 excited states of $[\text{Mn}(\text{imidazole})(\text{CO})_3(\text{phen})]^+$ associated to the a' imi modes (178, 195, 216, 254 cm^{-1}), a' CO modes (460, 646, 691 cm^{-1}), a' phen modes (471, 749, 1552, 1625, 1661 cm^{-1}) and a'' CO modes (95, 475, 637 cm^{-1}). Diagonal terms correspond to intrastate kappa obtained by means of the gradient computed at FC and off-diagonal terms correspond to interstate coupling lambda obtained within the overlap protocol of Ref. 26.

a' (imi)	S1 A''	S2 A'	S3 A'	S4 A''	S5 A'	S6 A'	S7 A''	S8 A''	S9 A'
S1 A''	0.0261								
S2 A'	0.0	0.0276							
S3 A'	0.0	0.0053	0.0417						
S4 A''	0.0527	0.0	0.0	0.1178					
S5 A'	0.0	0.0248	0.0234	0.0	0.0895				
S6 A'	0.0	0.0156	0.0175	0.0	0.0219	0.0309			
S7 A''	0.0117	0.0	0.0	0.0176	0.0	0.0	0.1022		
S8 A''	0.0032	0.0	0.0	0.0096	0.0	0.0	0.0318	0.1405	
S9 A'	0.0	0.0466	0.0181	0.0	0.0401	0.0239	0.0	0.0	0.0444
a' (CO)	S1 A''	S2 A'	S3 A'	S4 A''	S5 A'	S6 A'	S7 A''	S8 A''	S9 A'
S1 A''	0.0320								
S2 A'	0.0	0.0415							
S3 A'	0.0	0.0250	0.0489						
S4 A''	0.0365	0.0	0.0	0.1252					
S5 A'	0.0	0.0223	0.0343	0.0	0.0966				
S6 A'	0.0	0.0080	0.0141	0.0	0.0223	0.0517			
S7 A''	0.0201	0.0	0.0	0.0394	0.0	0.0	0.0607		
S8 A''	0.0067	0.0	0.0	0.0195	0.0	0.0	0.0155	0.0928	
S9 A'	0.0	0.0438	0.0139	0.0	0.0261	0.0239	0.0	0.0	0.0724
a' (phen)	S1 A''	S2 A'	S3 A'	S4 A''	S5 A'	S6 A'	S7 A''	S8 A''	S9 A'
S1 A''	0.1957								
S2 A'	0.0	0.2111							
S3 A'	0.0	0.0421	0.1466						
S4 A''	0.0616	0.0	0.0	0.1410					
S5 A'	0.0	0.0643	0.0849	0.0	0.1043				
S6 A'	0.0	0.0302	0.0161	0.0	0.0113	0.2391			
S7 A''	0.0060	0.0	0.0	0.0102	0.0	0.0	0.1163		
S8 A''	0.0120	0.0	0.0	0.0083	0.0	0.0	0.0338	0.1549	
S9 A'	0.0	0.0502	0.0300	0.0	0.0139	0.0233	0.0	0.0	0.1935
a'' (CO)	S1 A''	S2 A'	S3 A'	S4 A''	S5 A'	S6 A'	S7 A''	S8 A''	S9 A'
S1 A''	0.0								
S2 A'	0.0137	0.0							
S3 A'	0.0369	0.0	0.0						
S4 A''	0.0	0.0236	0.0108	0.0					
S5 A'	0.0179	0.0	0.0	0.0123	0.0				
S6 A'	0.0253	0.0	0.0	0.0555	0.0	0.0			
S7 A''	0.0	0.0069	0.0290	0.0	0.0190	0.0253	0.0		
S8 A''	0.0	0.0058	0.0167	0.0	0.0192	0.0038	0.0	0.0	
S9 A'	0.0025	0.0	0.0	0.0203	0.0	0.0	0.0293	0.0101	0.0

Table S5. Effective vibronic coupling (in eV) between the triplet T1-T9 excited states of $[\text{Mn}(\text{imidazole})(\text{CO})_3(\text{phen})]^+$ associated to the a' imi modes (178, 195, 216, 254 cm^{-1}), a' CO modes (460, 646, 691 cm^{-1}), a' phen modes (471, 749, 1552, 1625, 1661 cm^{-1}) and a'' CO modes (95, 475, 637 cm^{-1}). Diagonal terms correspond to intrastate kappa obtained by means of the gradient computed at FC and off-diagonal terms correspond to interstate coupling lambda obtained within the overlap protocol of Ref. 26.

a' (imi)	T1 A'	T2 A''	T3 A'	T4 A''	T5 A''	T6 A''	T7 A'	T8 A''	T9 A'
T1 A'	0.1426								
T2 A''	0.0	0.0925							
T3 A'	0.0158	0.0	0.0885						
T4 A''	0.0	0.0068	0.0	0.1606					
T5 A''	0.0	0.0590	0.0	0.0078	0.0370				
T6 A''	0.0	0.0331	0.0	0.0054	0.0541	0.1155			
T7 A'	0.0163	0.0	0.0604	0.0	0.0	0.0	0.0716		
T8 A''	0.0	0.0560	0.0	0.0058	0.0124	0.0315	0.0	0.0139	
T9 A'	0.0183	0.0	0.0468	0.0	0.0	0.0	0.0297	0.0	0.1131
a' (CO)	T1 A'	T2 A''	T3 A'	T4 A''	T5 A''	T6 A''	T7 A'	T8 A''	T9 A'
T1 A'	0.1116								
T2 A''	0.0	0.1083							
T3 A'	0.0233	0.0	0.0303						
T4 A''	0.0	0.0098	0.0	0.1435					
T5 A''	0.0	0.0335	0.0	0.0336	0.0468				
T6 A''	0.0	0.0455	0.0	0.0452	0.0722	0.1047			
T7 A'	0.0211	0.0	0.0385	0.0	0.0	0.0	0.0752		
T8 A''	0.0	0.0418	0.0	0.0146	0.0508	0.0137	0.0	0.0728	
T9 A'	0.0244	0.0	0.0460	0.0	0.0	0.0	0.0712	0.0	0.1035
a' (phen)	T1 A'	T2 A''	T3 A'	T4 A''	T5 A''	T6 A''	T7 A'	T8 A''	T9 A'
T1 A'	0.1275								
T2 A''	0.0	0.1373							
T3 A'	0.0231	0.0	0.1359						
T4 A''	0.0	0.0093	0.0	0.1636					
T5 A''	0.0	0.0496	0.0	0.0066	0.1199				
T6 A''	0.0	0.0027	0.0	0.0120	0.0690	0.1379			
T7 A'	0.0288	0.0	0.0591	0.0	0.0	0.0	0.1254		
T8 A''	0.0	0.0924	0.0	0.0115	0.1440	0.0738	0.0	0.1220	
T9 A'	0.0080	0.0	0.0446	0.0	0.0	0.0	0.0278	0.0	0.1245
a'' (CO)	T1 A'	T2 A''	T3 A'	T4 A''	T5 A''	T6 A''	T7 A'	T8 A''	T9 A'
T1 A'	0.0								
T2 A''	0.0548	0.0							
T3 A'	0.0	0.0216	0.0						
T4 A''	0.0368	0.0	0.0416	0.0					
T5 A''	0.0362	0.0	0.0269	0.0	0.0				
T6 A''	0.0481	0.0	0.0448	0.0	0.0	0.0			
T7 A'	0.0	0.0297	0.0	0.0664	0.0182	0.0110	0.0		
T8 A''	0.0510	0.0	0.0065	0.0	0.0	0.0	0.0066	0.0	
T9 A'	0.0	0.0251	0.0	0.0196	0.0234	0.0734	0.0	0.0242	0.0

Table S6. SOC terms (in cm^{-1} at the top, in meV at the bottom) at Franck Condon between the six lowest singlet and eight lowest triplet electronic excited states of $[\text{Re}(\text{imi})(\text{CO})_3(\text{phen})]^+$. Only one component is given.

cm^{-1}	S1	S2	S3	S4	S5	S6	T1	T2	T3	T4	T5	T6	T7
T1	0	329	-444	60	0	0							
	-2i	346i	159i	-239i	-32i	1i							
T2	126	0	0	0	-46	-32	109						
	368i	197i	-439i	120i	-66i	-55i	318i						
T3	0	-107	214	26	0	0	0	-56					
	4i	-40i	26i	275i	-80i	-27i	2i	-170i					
T4	585	0	0	0	103	-60	528	0	-201				
	47i	-407i	-246i	412i	140i	-9i	65i	453i	40i				
T5	-183	0	0	0	264	79	-136	0	118	0			
	121i	234i	-94i	-105i	421i	23i	177i	-170i	129i	-193i			
T6	0	-86	85	-41	0	0	0	-17	0	-128	1		
	8i	-113i	-76i	-14i	31i	8i	1i	-57i	-6i	-35i	-120i		
T7	-38	0	0	0	-63	-12	-34	0	2	0	0	15	
	356i	293i	-379i	21i	-87i	-51i	305i	-105i	-174i	-451i	127i	-52i	
T8	0	-224	-174	-354	0	0	0	67	0	-157	-406	0	91
	10i	-155i	-128i	-226i	-268i	2i	-60i	36i	-167i	-96i	-278i	78i	50i

meV	S1	S2	S3	S4	S5	S6	T1	T2	T3	T4	T5	T6	T7
T1	0	40.8	-55.0	7.4	0	0							
	-0.2i	42.9i	19.7i	-29.6i	-4.0i	0.1i							
T2	15.6	0	0	0	-5.7	-4.0	13.5i						
	45.6i	24.4i	-54.4i	14.9i	-8.2i	-6.8i	39.4i						
T3	0	-13.3	26.5	3.2	0	0	0	-6.9					
	0.5i	-5.0i	3.2i	34.1i	-9.9i	-3.3i	0.2i	-21.1i					
T4	72.5	0	0	0	12.8	-7.4	65.5	0	-24.9				
	5.8i	-50.5i	-30.5i	51.1i	17.4i	-1.1i	8.1i	56.2i	5.0i				
T5	-22.7	0	0	0	32.7	9.8	-16.9	0	14.6	0			
	15.0i	29.0i	-11.7i	-13.0i	52.2i	2.9i	21.9i	-21.1i	16.0i	-23.9i			
T6	0	-10.7	10.5	-5.1	0	0	0	-2.1	0.0	-15.9	0.1		
	1.0i	-14.0i	-9.4i	-1.7i	3.8i	1.0i	0.1i	-7.1i	-0.7i	-4.3i	-14.9i		
T7	-4.7	0	0	0	-7.8	-1.5	-4.2	0	0.2	0	0	1.9	
	44.1i	36.3i	-47.0i	2.6i	-10.8i	-6.3i	37.8i	-13.0i	-21.6i	-55.9i	15.7i	-6.4i	
T8	0	-27.8	-21.6	-43.9	0	0	0	8.3	0	-19.5	-50.3	0	11.3
	1.2i	-19.2i	-15.9i	-28.0i	-33.2i	0.2i	-7.4i	4.5i	-20.7i	-11.9i	-34.5i	9.7i	6.2i

Table S7. SOC terms (in cm^{-1} at the top, in meV at the bottom) at Franck Condon between the nine lowest singlet (S7 and S8 not included) and nine lowest triplet electronic excited states of $[\text{Mn}(\text{imi})(\text{CO})_3(\text{phen})]^+$. Only one component is given.

cm^{-1}	S1	S2	S3	S4	S5	S6	S9	T1	T2	T3	T4	T5	T6	T7	T8
T1	21	0	0	-84	0	0	0								
	8i	0i	8i	-65i	6i	17i	-4i								
T2	0	43	-55	0	-12	-28	-18	34							
	-18i	55i	29i	-11i	32i	-31i	-52i	21i							
T3	-34	0	0	43	0	0	0	0	24						
	-66i	-26i	85i	47i	35i	27i	-29i	26i	64i						
T4	0	-1	4	0	-4	-85	-30	89	0	-7					
	10i	6i	-4i	-45i	-4i	-34i	-12i	-24i	8i	-21i					
T5	0	-9	23	0	10	-10	-19	31	0	-7	0				
	-24i	-15i	-3i	37i	14i	-43i	-75i	-32i	20i	1i	-50i				
T6	0	4	12	0	12	63	-13	6	0	-26	0	0			
	-1i	0i	8i	56i	-13i	-68i	-38i	-86i	-13i	-24i	-101i	-7i			
T7	47	0	0	-55	0	0	0	0	-47	0	43	-5	29		
	-17i	-33i	1i	-36i	-15i	15i	23i	-42i	-5i	-88i	52i	-21i	4i		
T8	0	25	-42	0	0	43	6	-23	0	-1	0	0	0	13	
	21i	23i	2i	-7i	28i	-19i	43i	-20i	-34i	8i	-21i	-11i	1i	34i	
T9	-48	0	0	-7	0	0	0	0	67	0	10	22	18	0	12
	12i	70i	29i	-46i	41i	-43i	-57i	-9i	-31i	58i	-10i	-13i	32i	-58i	34i

meV	S1	S2	S3	S4	S5	S6	S9	T1	T2	T3	T4	T5	T6	T7	T8
T1	2.6	0	0	-10.4	0	0	0								
	1.0i	0i	1.0i	-8.1i	0.7i	2.1i	-0.5i								
T2	0.0	5.3	-6.8	0.0	-1.5	-3.5	-2.2	4.2							
	-2.2i	6.8i	3.6i	-1.4i	4.0i	-3.8i	-6.4i	2.6i							
T3	-4.2	0.0	0	5.3	0	0	0	0	3.0						
	-8.2i	-3.2i	10.5i	5.8i	4.3i	3.3i	-3.6i	3.2i	7.9i						
T4	0	-0.1	0.5	0.0	-0.5	-10.5	-3.7	11.0	0	-0.9					
	1.2i	0.7i	-0.5i	-5.6i	-0.5i	-4.2i	-1.5i	-3.0i	1.0i	-2.6i					
T5	0	-1.1	2.9	0	1.2	-1.2	-2.4	3.8	0	-0.9	0				
	-3.0i	-1.9i	-0.4i	4.6i	1.7i	-5.3i	-9.3i	-4.0i	2.5i	0.1i	-6.2i				
T6	0	0.5	1.5	0	1.5	7.8	-1.6	0.7	0	-3.2	0	0			
	-0.1i	0	1.0i	6.9i	-1.6i	-8.4i	-4.7i	-10.7i	-1.6i	-3.0i	-12.5i	-0.9i			
T7	5.8	0	0	-6.8	0	0	0	0	-5.8	0	5.3	-0.6	3.6		
	-2.1i	-4.1i	0.1i	-4.5i	-1.9i	1.9i	2.9i	-5.2i	-0.6i	-10.9i	6.4i	-2.6i	0.5i	0i	
T8	0	3.1	-5.2	0	0	5.3	0.7	-2.9	0	-0.1	0	0	0	1.6	
	2.6i	2.9i	0.2i	-0.9i	3.5i	-2.4i	5.3i	-2.5i	-4.2i	1.0i	-2.6i	-1.4i	0.1i	4.2i	
T9	-6.0	0	0	-0.9	0	0	0	0	8.3	0	1.2	2.7	2.2	0	1.5
	1.5i	8.7i	3.6i	-5.7i	5.1i	-5.3i	-7.1i	-1.1i	-3.8i	7.2i	-1.2i	-1.6i	4.0i	-7.2i	4.2i