

Supplementary Information

Spin-vibronic mechanism at work in a luminescent square-planar cyclometalated tridentate Pt(II) complex: absorption and ultrafast photophysics

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THEORY

Spin-vibronic Hamiltonian in n_{el} coupled diabatic electronic spin-free basis can be expressed as:¹⁻³

$$H(\mathbf{Q}) = (T_N + V_0(\mathbf{Q}))\mathbf{I} + \mathbf{W}^{VC}(\mathbf{Q}) + \mathbf{W}^{SOC}(\mathbf{Q}) \quad (\text{S1})$$

where T_N is the kinetic energy operator of the nucleus, $V_0(\mathbf{Q})$ is the potential energy of some reference electronic state and \mathbf{I} is the identity matrix with dimension $n_{el} \times n_{el}$. Here $V_0(\mathbf{Q})$ is determined from the electronic structure calculations at the ground state equilibrium geometry and taken as harmonic potential with vibrational frequencies ω_i along the set of dimensionless normal mode coordinates \mathbf{Q} . $\mathbf{W}^{VC}(\mathbf{Q})$ is the potential coupling matrix for the vibronic-coupling and $\mathbf{W}^{SOC}(\mathbf{Q})$ is the spin-orbit coupling matrix. The $\mathbf{W}^{VC}(\mathbf{Q})$ can be expand by Taylor series around the Franck-Condon (FC) point, $\mathbf{Q} = 0$:

$$W_{mn}^{VC}(\mathbf{Q}) = \varepsilon_n + \sum_i \kappa_i^{(n)} Q_i + \frac{1}{2} \sum_{ij} \gamma_{ij}^{(n)} Q_i Q_j + \dots \quad (\text{S2})$$

$$W_{nm}^{VC}(\mathbf{Q}) = \sum_i \lambda_i^{(n,m)} Q_i + \dots \quad (\text{S3})$$

$W_{nn}^{VC}(\mathbf{Q})$ is diagonal matrix element of the $\mathbf{W}^{VC}(\mathbf{Q})$ matrix. ε_n is the vertical excitation energy of the n th the electronic state. $\kappa_i^{(n)}$ and $\gamma_{ij}^{(n)}$ are the first and second order intra-state coupling constants for the Q_i mode. In the linear vibronic coupling (LVC) model we will neglect the $\gamma_{ij}^{(n)}$ and all the higher order terms. On the other hand, $W_{nm}^{VC}(\mathbf{Q})$ is the off-diagonal matrix element with the inter-state coupling constant $\lambda_i^{(n,m)}$.

$\kappa_i^{(n)}$ can be calculated from the gradient of adiabatic potential energy surface $V_n(\mathbf{Q})$ along a particular mode Q_i at FC point.

$$\kappa_i^{(n)} = \left. \frac{\partial V_n(\mathbf{Q})}{\partial Q_i} \right|_0 \quad (\text{S4})$$

$\kappa_i^{(n)}$ represents the force acting within an electronic surface and are responsible for shift in the potential minima for the excited state compared to the ground state minima, they are called tuning modes.

The $\lambda_i^{(n,m)}$ can be computed from the difference between hessian of the two adiabatic sates at FC point.

$$\lambda_i^{(n,m)} = \sqrt{\left. \frac{1}{8} \frac{\partial^2 (V_n(\mathbf{Q}) - V_m(\mathbf{Q}))^2}{\partial Q_i^2} \right|_0} \quad (\text{S5})$$

$\lambda_i^{(n,m)}$ s are responsible for the nonadiabatic transition between two electronic states.

Alternatively, beyond the pair of states approximation, $\lambda_i^{(n,m)}$ can be evaluated from the overlaps between electronic wavefunctions at close-lying geometries. The $W_{nm}^{VC}(\mathbf{Q})$ matrix in Eq. (S3) can be expresses as

$$W_{nm}^{VC}(\mathbf{Q}) = \langle \Phi_n | H_{\text{el}} | \Phi_m \rangle \quad (\text{S6})$$

where H_{el} is the electronic Hamiltonian and Φ_n is the n th diabatic electronic state. Consequently, $\lambda_i^{(n,m)}$ can be defined as⁴

$$\lambda_i^{(n,m)} = \left. \frac{\partial W_{nm}^V(\mathbf{Q})}{\partial Q_i} \right|_0 = \left. \frac{\partial \langle \Phi_n | H_{\text{el}} | \Phi_m \rangle}{\partial Q_i} \right|_0 \quad (\text{S7})$$

For each normal mode i of interest, energy $E_n(\delta Q_i)$ of the adiabatic wavefunction $\Psi_n(\delta Q_i)$ is calculated at finite displacement of the geometry δQ_i . Additionally, the overlap between the $\Psi_n(0)$ and $\Psi_n(\delta Q_i)$ is calculated

$$S_i^{nm} = \langle \Psi_n(0) | \Psi_m(\delta Q_i) \rangle \quad (\text{S8})$$

Afterwards, an adiabatic-to-diabatic transformation matrix U is constructed by a Löwdin orthogonalization⁵ of the overlap matrix S . The diabatic Hamiltonian at the displaced geometry is obtained as^{6,7}

$$\mathbf{W}^V(\delta Q_i) = U \begin{pmatrix} E_1(\delta Q_i) & \cdots & 0 \\ \vdots & \ddots & \vdots \\ 0 & \cdots & E_n(\delta Q_i) \end{pmatrix} U^T \quad (\text{S9})$$

The $\lambda_i^{(n,m)}$ values are computed by a numerical differentiation

$$\lambda_i^{(n,m)} = \frac{\partial W_{nm}^V(\delta Q_i)}{\delta Q_i} \quad (\text{S10})$$

We can deduce some selection rules for calculating the $\kappa_i^{(n)}$ and $\lambda_i^{(n,m)}$. To get the nonzero matrix elements for the coupling constants the direct product of the irreducible representation of the vibrational mode, Γ_Q and electronic state Γ_n and Γ_m should contain the totally symmetric representation Γ_A .

$$\Gamma_n \otimes \Gamma_Q \otimes \Gamma_m \supset \Gamma_A \quad (\text{S11})$$

All totally symmetric modes will produce nonzero values for $\kappa_i^{(n)}$.

The spin-orbit coupling matrix $\mathbf{W}^{SOC}(\mathbf{Q})$ is also depend on nuclear coordinates (\mathbf{Q}), but for simplicity we take constant value at FC geometry $\mathbf{W}^{SOC}(\mathbf{0})$. Spin-orbit coupling causes the radiationless singlet-triplet transition. For nine state (lowest five triplet and lowest four singlet) problem in our case the $\mathbf{W}^{VC}(\mathbf{Q})$ and $\mathbf{W}^{SOC}(\mathbf{0})$ can be combinedly written as a 19×19 matrix (explicitly considering each triple as three states):

$$\mathbf{W}(\mathbf{Q}) = \mathbf{W}^{VC}(\mathbf{Q}) + \mathbf{W}^{SOC}(\mathbf{0}) = \begin{pmatrix} W_{T1,T1} & W_{T1,T2} & W_{T1,T3} & W_{T1,S1} & W_{T1,S2} & W_{T1,T4} & W_{T1,T5} & W_{T1,S3} & W_{T1,S4} \\ W_{T1,T2}^* & W_{T2,T2} & W_{T2,T3} & W_{T2,S1} & W_{T2,S2} & W_{T2,T4} & W_{T2,T5} & W_{T2,S3} & W_{T2,S4} \\ W_{T1,T3}^* & W_{T2,T3}^* & W_{T3,T3} & W_{T3,S1} & W_{T3,S2} & W_{T3,T4} & W_{T3,T5} & W_{T3,S3} & W_{T3,S4} \\ W_{T1,S1}^* & W_{T2,S1}^* & W_{T3,S1}^* & W_{S1,S1} & W_{S1,S2} & W_{S1,T4} & W_{S1,T5} & W_{S1,S3} & W_{S1,S4} \\ W_{T1,S2}^* & W_{T2,S2}^* & W_{T3,S2}^* & W_{S1,S2}^* & W_{S2,S2} & W_{S2,T4} & W_{S2,T5} & W_{S2,S3} & W_{S2,S4} \\ W_{T1,T4}^* & W_{T2,T4}^* & W_{T3,T4}^* & W_{S1,T4}^* & W_{S2,T4}^* & W_{T4,T4} & W_{T4,T5} & W_{T4,S3} & W_{T4,S4} \\ W_{T1,T5}^* & W_{T2,T5}^* & W_{T3,T5}^* & W_{S1,T5}^* & W_{S2,T5}^* & W_{T4,T5}^* & W_{T5,T5} & W_{T5,S3} & W_{T5,S4} \\ W_{T1,S3}^* & W_{T2,S3}^* & W_{T3,S3}^* & W_{S1,S3}^* & W_{S2,S3}^* & W_{T4,S3}^* & W_{T5,S3}^* & W_{S3,S3} & W_{S3,S4} \\ W_{T1,S4}^* & W_{T2,S4}^* & W_{T3,S4}^* & W_{S1,S4}^* & W_{S2,S4}^* & W_{T4,S4}^* & W_{T5,S4}^* & W_{S3,S4}^* & W_{S4,S4} \end{pmatrix} \quad (\text{S12})$$

where the asterisk stands for the conjugate transpose. Considering the triplet component explicitly $\mathbf{W}(\mathbf{Q})$ have the submatrices

$$W_{nn} = \epsilon_n + \sum_{i \in A'} \kappa_i^{(n)} Q_i; \quad W_{S_n(A'), S_m(A'')} = \sum_{i \in A''} \lambda_i^{S_n, S_m} Q_i; \quad (\text{S13})$$

$$W_{S_n(A'), S_m(A')} = W_{S_n(A''), S_m(A'')} = \sum_{i \in A'} \lambda_i^{S_n, S_m} Q_i; \quad (\text{S14})$$

$$W_{S_n(A'), T_m(A')} = W_{S_n(A''), T_m(A'')} = \begin{pmatrix} 0 & \eta^{S_n/T_m} & 0 \end{pmatrix}; \quad (\text{S15})$$

$$W_{S_n(A'), T_m(A'')} = W_{S_n(A''), T_m(A')} = \begin{pmatrix} \eta^{*S_n/T_m} & 0 & \eta^{S_n/T_m} \end{pmatrix}; \quad (\text{S16})$$

$$W_{T_n(A'), T_m(A')} = W_{T_n(A''), T_m(A'')} \begin{pmatrix} \sum_{i \in A'} \lambda_i^{T_1, T_3} Q_i + \eta^{T_n/T_m} & 0 & 0 \\ 0 & \sum_{i \in A'} \lambda_i^{T_1, T_3} Q_i & 0 \\ 0 & 0 & \sum_{i \in A'} \lambda_i^{T_1, T_3} Q_i + \eta^{*T_n/T_m} \end{pmatrix}; \quad (\text{S17})$$

$$W_{T_n(A'), T_m(A'')} = \begin{pmatrix} \sum_{i \in A''} \lambda_i^{T_n, T_m} Q_i & \eta^{T_n/T_m} & 0 \\ -\eta^{*T_n/T_m} & \sum_{i \in A''} \lambda_i^{T_n, T_m} Q_i & \eta^{T_n/T_m} \\ 0 & -\eta^{*T_n/T_m} & \sum_{i \in A''} \lambda_i^{T_n, T_m} Q_i \end{pmatrix} \quad (\text{S18})$$

The sub-matrixes goes from ascending order of magnetic quantum number. ϵ_n is the vertical excitation energy of the spin-free electronic state n . The zero values in the sub-matrixes W_{nm} are due to symmetry reason. The $\eta^{n/m}$ is the spin-orbit coupling constant obtained from the electronic structure calculation using TDDFT. All the constant used to construct the Hamiltonian in Eq. (S1) are presented in Table S6.

TABLE S1: Important geometrical parameters for the optimized structure of the Pt (II) complex

Parameters	Calculated (Å)	Expt (Å) ⁸
Pt(1)-C(30)	1.927	1.903
Pt(1)-N(3)	2.068	2.035
Pt(1)-N(4)	2.068	2.036
Pt(1)-Cl(2)	2.494	2.405
N(3)-Pt(1)-N(4)	160.4	161.29
C(30)-Pt(1)-Cl(2)	180.0	178.30
C(30)-Pt(1)-N(3)	80.2	80.63
C(1)-Pt(1)-N(4)	80.2	80.68

TABLE S2: Calculated frequencies (in cm^{-1}) at the optimized ground state geometry.

mode	ω	mode	ω	mode	ω	mode	ω	mode	ω
$Q_1(A'')$	8.290	$Q_2(A')$	34.851	$Q_3(A')$	55.740	$Q_4(A'')$	85.142	$Q_5(A')$	92.193
$Q_7(A'')$	127.164	$Q_8(A')$	143.300	$Q_9(A')$	170.017	$Q_{10}(A'')$	180.861	$Q_{11}(A')$	229.507
$Q_{13}(A'')$	251.223	$Q_{14}(A')$	255.266	$Q_{15}(A')$	288.135	$Q_{16}(A')$	315.298	$Q_{17}(A'')$	332.958
$Q_{19}(A'')$	381.816	$Q_{20}(A'')$	422.516	$Q_{21}(A')$	437.475	$Q_{22}(A')$	447.899	$Q_{23}(A'')$	458.049
$Q_{25}(A')$	579.828	$Q_{26}(A'')$	596.894	$Q_{27}(A'')$	602.483	$Q_{28}(A')$	636.196	$Q_{29}(A'')$	656.164
$Q_{31}(A')$	676.722	$Q_{32}(A')$	699.275	$Q_{33}(A')$	733.785	$Q_{34}(A'')$	757.478	$Q_{35}(A')$	763.823
$Q_{37}(A')$	794.754	$Q_{38}(A'')$	851.016	$Q_{39}(A')$	882.420	$Q_{40}(A'')$	901.380	$Q_{41}(A')$	903.067
$Q_{43}(A'')$	921.004	$Q_{44}(A'')$	992.610	$Q_{45}(A')$	993.206	$Q_{46}(A'')$	1014.391	$Q_{47}(A')$	1014.436
$Q_{49}(A')$	1035.936	$Q_{50}(A'')$	1036.403	$Q_{51}(A')$	1059.096	$Q_{52}(A')$	1062.501	$Q_{53}(A'')$	1071.297
$Q_{55}(A'')$	1113.520	$Q_{56}(A')$	1118.521	$Q_{57}(A')$	1142.763	$Q_{58}(A'')$	1181.510	$Q_{59}(A')$	1181.718
$Q_{61}(A')$	1199.148	$Q_{62}(A')$	1255.188	$Q_{63}(A'')$	1263.568	$Q_{64}(A'')$	1293.592	$Q_{65}(A'')$	1308.220
$Q_{67}(A'')$	1335.737	$Q_{68}(A')$	1357.547	$Q_{69}(A')$	1412.060	$Q_{70}(A')$	1435.979	$Q_{71}(A'')$	1440.837
$Q_{73}(A')$	1480.277	$Q_{74}(A'')$	1482.590	$Q_{75}(A')$	1486.981	$Q_{76}(A')$	1500.461	$Q_{77}(A'')$	1505.284
$Q_{79}(A')$	1589.856	$Q_{80}(A'')$	1601.424	$Q_{81}(A')$	1621.692	$Q_{82}(A'')$	1637.169	$Q_{83}(A')$	1638.581
$Q_{85}(A')$	3070.894	$Q_{86}(A'')$	3098.855	$Q_{87}(A'')$	3158.849	$Q_{88}(A')$	3160.207	$Q_{89}(A'')$	3178.556
$Q_{91}(A')$	3191.104	$Q_{92}(A'')$	3191.159	$Q_{93}(A'')$	3197.702	$Q_{94}(A')$	3197.805	$Q_{95}(A'')$	3204.350
								$Q_{96}(A')$	3205.070

TABLE S3: SOC matrix elements (calculated as root mean square in cm^{-1}) between the low-lying singlet and triplet states of $[\text{Pt}(\text{dpybMe})\text{Cl}]$.

	T1	T2	T3	T4	T5	T6	T7	T8	T9	T10
$\langle S H_{\text{So}} T\rangle$										
S1:	0.56	62.43	1.48	843.22	1883.80	647.31	93.83	1121.89	1.72	395.48
S2:	69.16	0.27	438.89	1.27	205.70	2.79	1702.72	685.47	795.39	2.68
S3:	1696.46	163.57	791.31	1994.72	0.24	1294.01	30.47	161.90	138.46	1281.71
S4:	765.81	2.90	292.14	6.05	2071.24	1.13	355.79	970.97	12.30	10.36
S5:	55.51	1530.91	1082.04	572.46	48.81	315.41	1.70	1.45	1986.68	378.66
S6:	960.31	331.45	249.36	908.79	165.53	617.56	1.22	2.70	280.94	672.57
S7:	7.72	847.22	16.89	285.93	11.43	39.90	2323.34	824.74	26.74	183.58
S8:	256.26	0.87	46.28	2.57	497.77	1.82	300.11	198.99	241.74	0.36
S9:	171.12	911.25	469.42	197.23	1.64	113.62	146.81	123.90	962.42	317.41
S10:	702.06	1.73	284.32	6.48	1950.01	6.33	480.16	892.18	15.55	2.97
$\langle T H_{\text{So}} T\rangle$										
T1:	0.00	63.36	1.81	1007.90	2357.98	583.80	157.96	1368.94	3.13	708.30
T2:	63.36	0.00	573.88	1.31	224.77	3.86	2040.44	829.19	973.99	3.88
T3:	1.81	573.88	0.00	385.21	1087.41	189.68	1571.53	97.68	6.50	485.91
T4:	1007.90	1.31	385.21	0.00	2781.81	3.37	999.48	1109.15	109.86	11.59
T5:	2357.98	224.77	1087.41	2781.81	0.00	1803.42	161.22	164.11	221.80	1785.54
T6:	583.80	3.86	189.68	3.37	1803.42	0.00	625.31	759.90	258.76	11.29
T7:	157.96	2040.44	1571.53	999.48	161.22	625.31	0.00	9.95	2708.74	403.39
T8:	1368.94	829.19	97.68	1109.15	164.11	759.90	9.95	0.00	856.89	1053.88
T9:	3.13	973.99	6.50	109.86	221.80	258.76	2708.74	856.89	0.00	516.44
T10:	708.30	3.88	485.91	11.59	1785.54	11.29	403.39	1053.88	516.44	0.00

TABLE S4: TD-DFT/B3LYP transition energies (in eV) without spin-orbit coupling to the low-lying singlet and triplet excited states of [Pt(dpybMe)Cl], absorption wavelengths (in nm) and associated oscillator strengths (f). The labels are based on dominant contributions.

Label	State	Energy (eV)	Wavelength (nm)	f
LC / MLCT	S1 (A')	3.17159	390.91	0.0056
LC / MLCT	S2 (A'')	3.17732	390.20	0.3013
MLCT	S3 (A')	3.62561	341.96	0.0239
LC / MLCT	S4 (A'')	3.63159	341.39	0.0086
MLCT	S5 (A'')	3.76071	329.67	0.0000
MLCT / XLCT	S6 (A'')	3.82990	323.72	0.0000
LC / MLCT	S7 (A')	3.94260	314.46	0.1702
LC / MLCT	S8 (A'')	3.95111	313.79	0.0003
MLCT / XLCT	S9 (A')	3.98974	310.75	0.0003
LC / MLCT	S10 (A'')	4.13702	299.68	0.6798
LC / MLCT	S11 (A')	4.27430	290.06	0.1669
LC / MLCT	S12 (A')	4.30301	288.12	0.2240
LC / MLCT / LMCT / MC	S13 (A')	4.38446	282.77	0.0002
MLCT	S14 (A'')	4.54979	272.50	0.0000
LC / XLCT	S15 (A')	4.56407	271.64	0.0559
LC / XLCT	S16 (A'')	4.57962	270.72	0.0960
LC / MLCT	S17 (A')	4.63061	267.74	0.0063
MLCT / XLCT	S18 (A')	4.73970	261.58	0.0002
LC / MLCT	S19 (A'')	4.82736	256.83	0.5320
MLCT	S20 (A')	4.84708	255.78	0.0086
LC / MLCT	T1 (A')	2.75759	449.60	0.0000
LC / MLCT	T2 (A'')	2.79256	443.97	0.0000
LC	T3 (A')	3.15250	393.28	0.0000
LC / MLCT	T4 (A'')	3.31840	373.61	0.0000
MLCT	T5 (A')	3.46361	357.95	0.0000
LC / MLCT	T6 (A'')	3.65718	339.00	0.0000
MLCT	T7 (A'')	3.73263	332.15	0.0000
MLCT / XLCT	T8 (A'')	3.77580	328.35	0.0000
LC / MLCT	T9 (A')	3.82513	324.12	0.0000
LC / MLCT	T10 (A'')	3.85850	321.32	0.0000
LC / MLCT	T11 (A')	3.94068	314.62	0.0000
MLCT / XLCT	T12 (A')	3.96048	313.04	0.0000
LC / MLCT / LMCT / MC	T13 (A')	4.01949	308.45	0.0000
LC / MLCT	T14 (A')	4.11696	301.14	0.0000
MC / MLCT	T15 (A')	4.26061	290.99	0.0000
LC	T16 (A'')	4.28503	289.33	0.0000
MC / MLCT	T17 (A'')	4.34098	285.60	0.0000
LC / MLCT	T18 (A')	4.38271	282.88	0.0000
LC / XLCT	T19 (A'')	4.42401	280.24	0.0000
LC / MLCT	T20 (A')	4.42920	279.92	0.0000

TABLE S5: TD-DFT/B3LYP transition energies (in eV) with spin-orbit coupling to the low-lying excited states of [Pt(dpybMe)Cl], absorption wavelengths (in nm) and associated oscillator strengths (f).

State	Energy (eV)	Wavelength (nm)	f
1 (A'')	2.66777	464.73	0.0000
2 (A'')	2.66819	464.66	0.0009
3 (A')	2.67323	463.78	0.0009
4 (A'')	2.72914	454.28	0.0000
5 (A')	2.72918	454.28	0.0000
6 (A')	2.73044	454.07	0.0007
7 (A')	2.99532	413.91	0.0045
8 (A'')	3.04658	406.95	0.2086
9 (A'')	3.06784	404.13	0.0000
10 (A')	3.07369	403.36	0.0004
11 (A')	3.08981	401.25	0.0001
12 (A'')	3.09186	400.99	0.0485
13 (A'')	3.09268	400.88	0.0011
14 (A')	3.11641	397.83	0.0067
15 (A'')	3.21362	385.80	0.0436
16 (A')	3.45978	358.35	0.0536
17 (A')	3.48560	355.69	0.0001
18 (A'')	3.49261	354.98	0.0001
19 (A'')	3.49303	354.94	0.0061
20 (A'')	3.50482	353.74	0.0000
21 (A')	3.51928	352.29	0.0039
22 (A')	3.53269	350.95	0.0036
23 (A'')	3.61856	342.62	0.0000
24 (A')	3.64689	339.96	0.0045
25 (A'')	3.65471	339.23	0.0026
26 (A')	3.65859	338.87	0.0094
27 (A')	3.70939	334.23	0.0008
28 (A'')	3.72561	332.78	0.0000
29 (A')	3.75408	330.25	0.0028
30 (A'')	3.75785	329.92	0.0052

TABLE S6: List of the Parameters Entering the Model Hamiltonian. All the parameters are given in eV.

mode (A')	ω	κ^{S1}	κ^{S2}	κ^{S3}	κ^{S4}	κ^{T1}	κ^{T2}	κ^{T3}	κ^{T4}	κ^{T5}	$\lambda^{T1,T3}$
Q_2	0.004	0.002	0.001	0.001	0.001	0.002	0.001	0.001	0.001	0.001	0.0
Q_8	0.018	-0.010	-0.005	-0.003	-0.002	-0.004	-0.005	0.007	-0.008	-0.006	0.0
Q_{11}	0.028	0.034	0.034	-0.010	-0.009	0.022	0.027	0.001	-0.007	-0.012	0.012
Q_{15}	0.036	0.031	0.027	0.009	-0.022	0.029	0.028	-0.022	-0.018	0.009	0.016
Q_{32}	0.087	0.039	0.027	0.032	0.043	0.040	0.031	0.030	0.050	0.030	0.0
Q_{49}	0.128	-0.050	-0.029	-0.039	-0.086	-0.047	-0.030	-0.058	-0.094	-0.040	0.011
Q_{62}	0.156	-0.040	-0.038	-0.006	-0.008	-0.036	-0.032	-0.016	-0.014	-0.004	0.0
Q_{68}	0.168	-0.052	-0.086	-0.045	-0.081	-0.086	-0.109	-0.106	-0.069	-0.050	0.014
Q_{75}	0.184	-0.022	-0.056	0.002	-0.005	-0.049	-0.061	-0.021	-0.006	-0.004	0.0
Q_{76}	0.186	0.036	0.050	0.059	0.097	0.056	0.058	0.081	0.103	0.060	0.018
Q_{81}	0.201	0.051	-0.024	-0.035	-0.077	0.042	-0.040	-0.179	-0.064	-0.031	0.012
Q_{83}	0.203	0.064	-0.057	0.053	0.052	0.009	-0.070	-0.057	0.055	0.045	0.039

mode (A'')	ω	$\lambda^{S1,S2}$	$\lambda^{S1,S4}$	$\lambda^{S2,S3}$	$\lambda^{T1,T2}$	$\lambda^{T1,T4}$	$\lambda^{T2,T3}$	$\lambda^{T3,T4}$
Q_{50}	0.128	0.044	0.016	0.005	0.036	0.017	0.004	0.047
Q_{60}	0.147	0.035	0.004	0.012	0.020	0.008	0.013	0.037
Q_{64}	0.160	0.044	0.029	0.004	0.073	0.031	0.002	0.037
Q_{77}	0.187	0.071	0.023	0.008	0.085	0.041	0.001	0.077
Q_{78}	0.196	0.075	0.040	0.006	0.113	0.048	0.043	0.074
Q_{80}	0.199	0.011	0.052	0.010	0.077	0.024	0.071	0.009

State	E	η			
S1 (A')	3.172	S1/T4	0.0 - 0.074 i	S4/T3	0.0 + 0.026 i
S2 (A'')	3.177	S1/T5	0.0 + 0.234 i	S4/T5	-0.182 - 0.001 i
S3 (A')	3.626	S2/T3	-0.0 + 0.038 i	T1/T4	0.0 - 0.062 i
S4 (A'')	3.632	S2/T5	-0.018 + 0.0 i	T1/T5	0.0 + 0.207 i
T1 (A')	2.758	S3/T1	0.0 - 0.21 i	T2/T3	0.0 + 0.036 i
T2 (A'')	2.793	S3/T2	0.014 + 0.0 i	T2/T5	0.014 - 0.0 i
T3 (A')	3.152	S3/T3	0.0 + 0.098 i	T3/T4	0.0 + 0.024 i
T4 (A'')	3.318	S3/T4	-0.175 - 0.001 i	T3/T5	0.0 - 0.095 i
T5 (A')	3.464	S4/T1	-0.0 - 0.067 i	T4/T5	0.172 + 0.001 i

TABLE S7: Number of primitive basis and SPF for different mode combination used in the MCTDH calculation for the lowest 19 electronic states of the of [Pt(dpybMe)Cl] Complex using the 18-mode model Hamiltonian.

Modes	Primitive basis	SPF basis
(Q_2, Q_8, Q_{11})	(13,13,13)	(7, 7, 7, 7, 7, 7, 7, 7, 7, 7, 7)
(Q_{15}, Q_{32}, Q_{49})	(13,13,13)	(7, 7, 7, 7, 7, 7, 7, 7, 7, 7, 7)
(Q_{62}, Q_{68}, Q_{75})	(13,13,13)	(7, 7, 7, 7, 7, 7, 7, 7, 7, 7, 7)
(Q_{76}, Q_{81}, Q_{83})	(13,13,13)	(7, 7, 7, 7, 7, 7, 7, 7, 7, 7, 7)
(Q_{50}, Q_{60}, Q_{64})	(13,13,13)	(7, 7, 7, 7, 7, 7, 7, 7, 7, 7, 7)
(Q_{77}, Q_{78}, Q_{80})	(13,13,13)	(7, 7, 7, 7, 7, 7, 7, 7, 7, 7, 7)

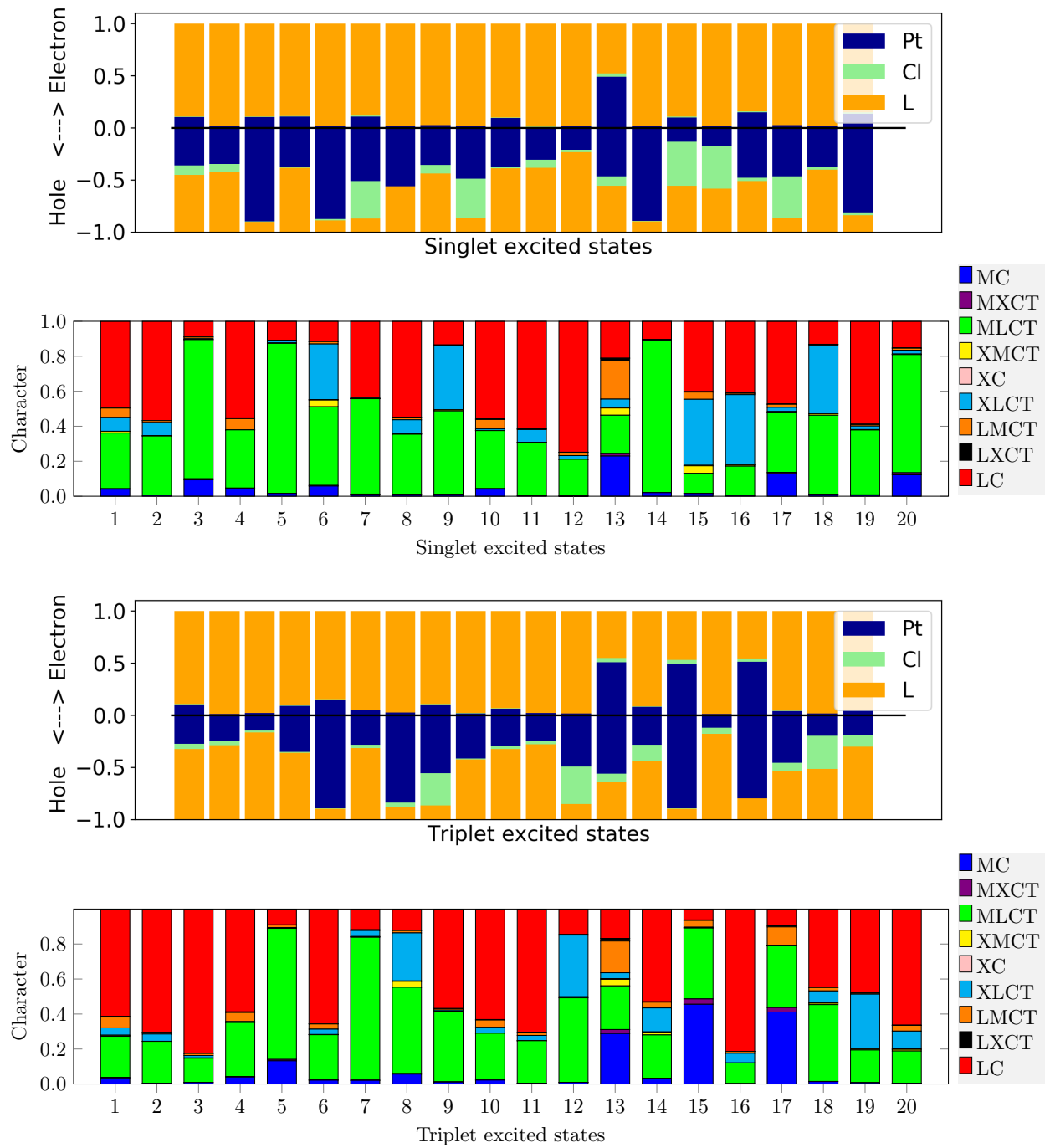


FIG. S1: TheoDORE analysis of low-lying singlet(top two panels) and triplet (bottom two panels) excited states calculated at the TD-DFT level at Franck-Condon.

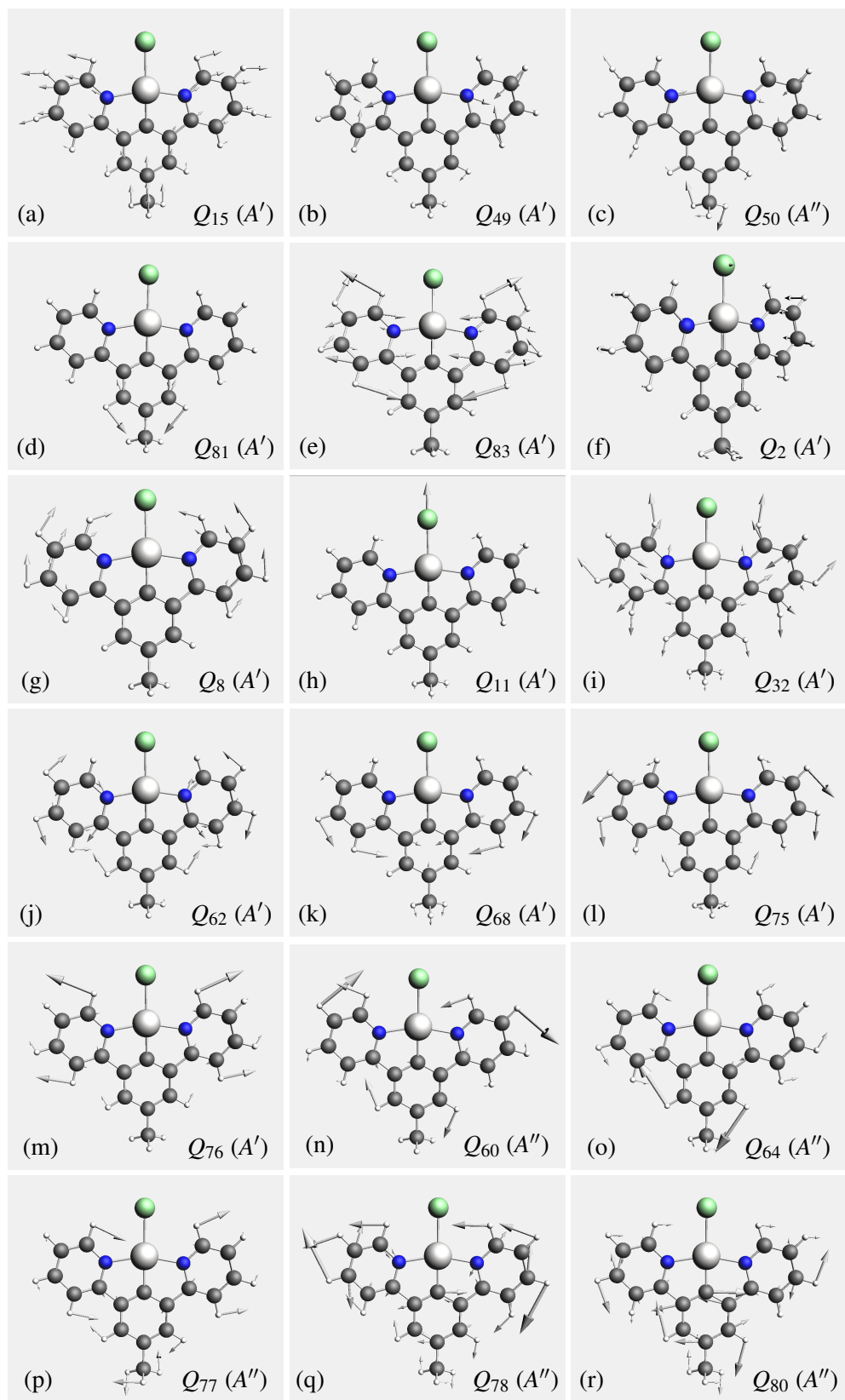


FIG. S2: (a)-(e) depict "metal-carbon and metal- nitrogen bond stretching" modes and (f)-(r) depict "ligand localized in-plane bending" modes.

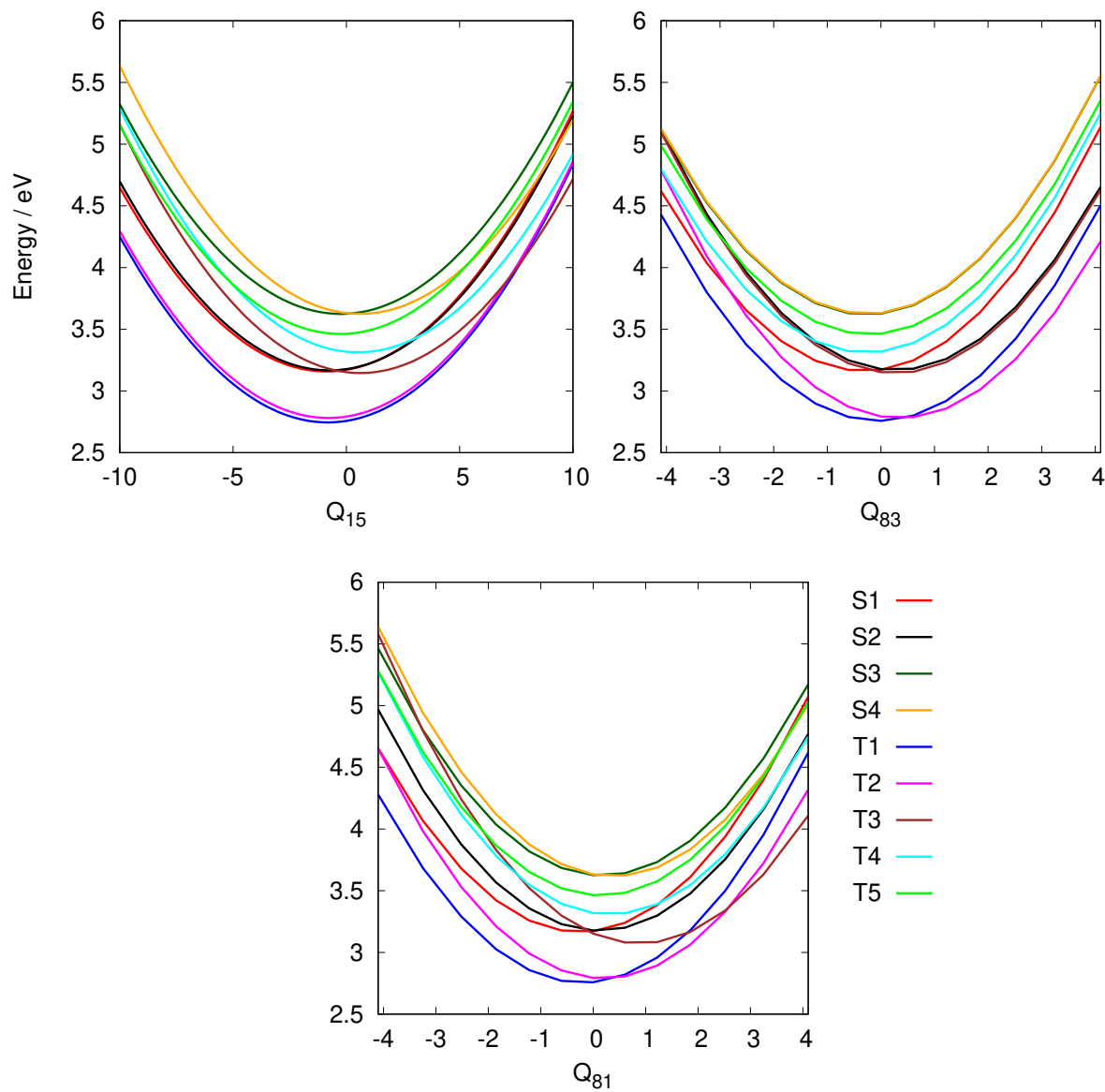


FIG. S3: 1D cut of diabatic potential along Q_{15} , Q_{83} and Q_{81} modes.

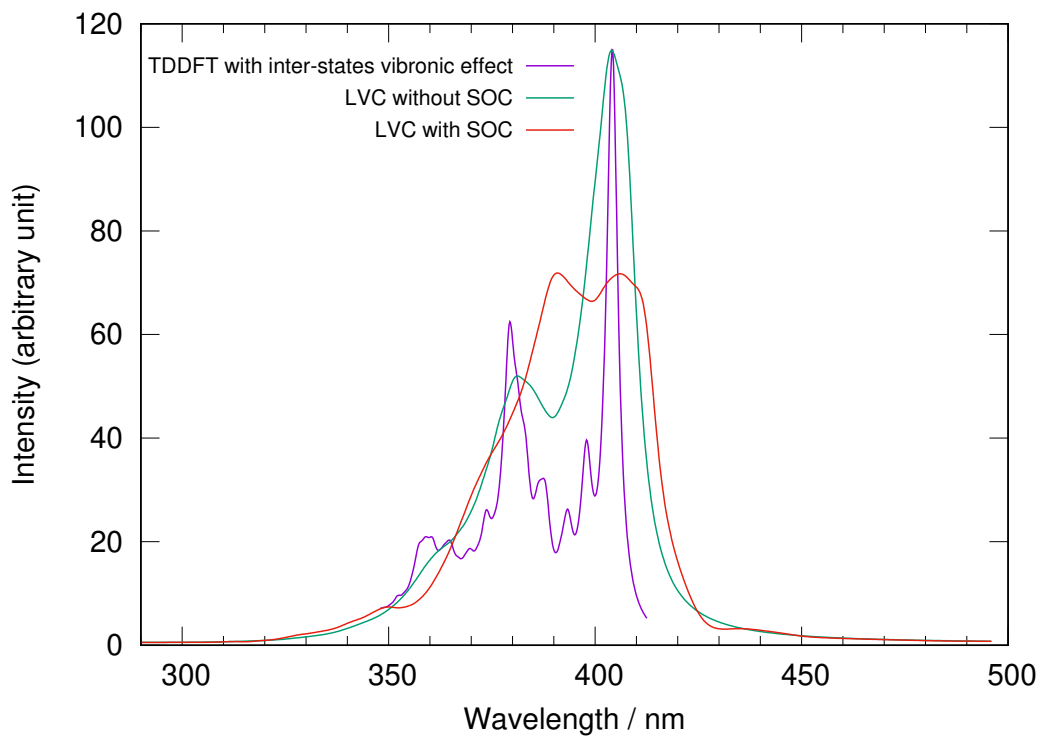


FIG. S4: Comparison of MCTDH calculated spectra with TDDFT vibronic spectra.

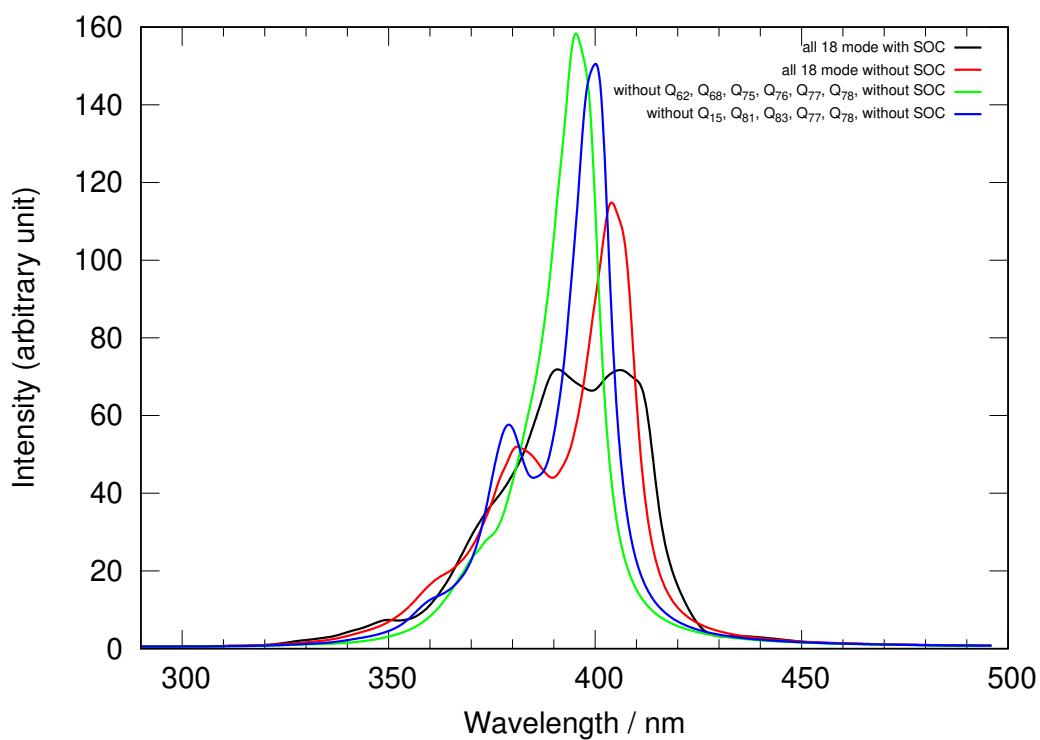


FIG. S5: Effect of different mode and SOC on the calculated spectra from MCTDH.

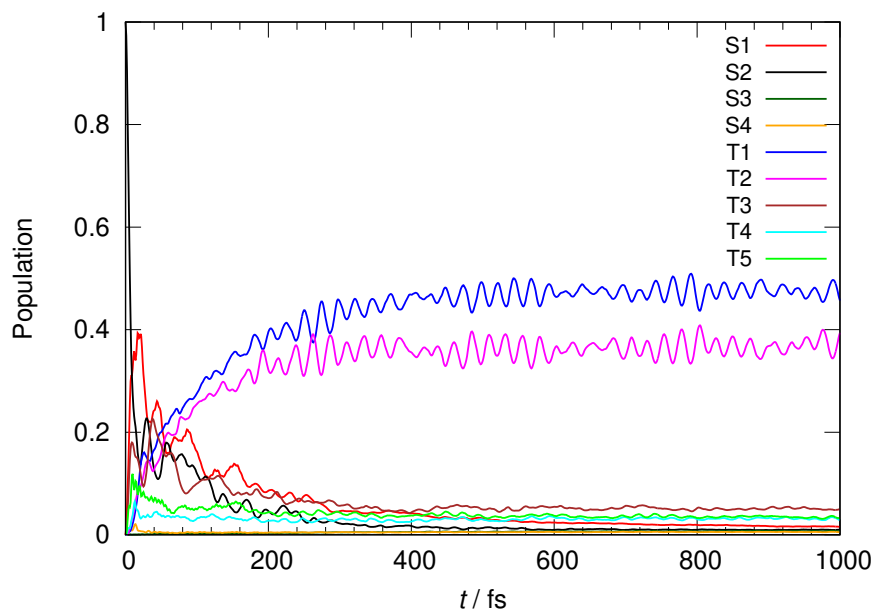


FIG. S6: Time evolution of the diabatic excited state population of [Pt(dpybMe)Cl] after visible light irradiation within 1 ps.

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