Electronic Supplementary Information:

DFT/TD-DFT Study of Electronic and Phosphorescent Properties in Cycloplatinated Complexes: Implications for OLEDs

Batool Moradpour and Reza Omidyan
Department of Chemistry, University of Isfahan, 81746-73441 Isfahan, Iran.

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Theoretical Background

According to the Marcus–Hush model, the rate of intermolecular charge transfer ($K_{ET}$) can be estimated by using the semi-classical Marcus theory as follows:

$$K_{ET} = \frac{4\pi}{h} \frac{1}{\sqrt{4\pi \lambda k_B T}} \beta^2 \exp\left(-\frac{\lambda}{4k_B T}\right)$$  \hspace{1cm} (1)

where $\beta$ is the transfer integral between the neighboring molecules, $T$ is the temperature, $h$ and $k_B$ are the Planck and Boltzmann constants respectively and $\lambda$ is the reorganization which plays a key role in the charge transfer rate for OLEDs $^1$. $\lambda$ Contains the internal reorganization ($\lambda_{in}$) and the outer reorganization energy ($\lambda_{out}$), namely, $\lambda = (\lambda_{in}) + (\lambda_{out})$. The carrier transferring process takes place in crystals or in amorphous films, which contributes to a smaller and even negligible $\lambda_{out}$. Getting a better insight into $\lambda$ and the transport mechanism of holes and electrons, the energy barrier for hole injection and electron injection is estimated using the ionization potentials ($IPs$) and the electronic affinities ($EAs$), respectively. The $IPs$ and $EAs$ are both obtained from vertical ($ver$, at the geometry of the neutral molecule) and adiabatic ($ad$, optimized structures for both the neutral and charged molecules). Also, based on the literature, the hole extraction potentials and the electron extraction potentials have been abbreviated as HEP and EEP, respectively $^2$.

Furthermore, efficient charge transfer depends mostly upon to the reorganization energy, $\lambda$ value, determined based on the following equations:

$$\lambda_h = [E^+(M) - E^+(M^+)] + [E(M^+) - E(M)]$$
$$= [E^+(M) - E(M)] - [E^+(M^+) - E(M^+)] = IP(\text{ver}) - HEP$$  \hspace{1cm} (2)

$$\lambda_e = [E^-(M) - E^-(M^-)] + [E(M^-) - E(M)]$$
$$= [E(M^-) - E^-(M^-)] - [E(M) - E^-(M)] = EEP - EA(\text{ver})$$  \hspace{1cm} (3)

Where $E(M)$ and $E^\pm (M^\pm)$ represent the energies of the neutral and cation/anion species in their lowest energy geometry respectively, while $E(M^\pm)$ and $E^\pm (M)$ represent the energies of the cation (or onion) and neutral geometries respectively $^1,2$. $\lambda_h$ and $\lambda_e$ represent the relevant hole-
and electron reorganization energy. The lower difference value between these two parameters, the better charge balance between holes and electrons.

**Phosphorescence quantum yield** $\Phi_p$

In general, phosphorescence quantum efficiency $\Phi_p$ is governed by three processes: 1) singlet-triplet intersystem crossing (ISC), 2) radiative decay from a triplet state to the singlet ground state, and 3) non-radiative decay from an excited state to the ground state. To obtain strong emitters, processes 1) and 2) must be fast, and process 3) slow. The ISC quantum yield is assumed to be unity.

Phosphorescence quantum yield $\Phi_p$ is directly related to the radiative rate constant (K$_r$) and emission decay time ($\tau_{em}$) and is expressed as

$$\Phi_p = K_r \tau_{em} = K_r + K_{nr}$$  \hspace{1cm} (1)

Where $\tau_{em} = \frac{1}{K_r + K_{nr}}$, and $K_{nr}$ represents the non-radiative decay rate including temperature-independent and -dependent$^3,4$.

**The radiative decay rate constant** (K$_r$)

Within the Born–Oppenheimer approximation, the radiative decay rate constant K$_r$ from the $m^{th}$ triplet excited state $T_m$ (usually $m=1$ according to the Kasha rule) to the singlet ground state ($S_0$) can be expressed as Equation (2)$^5$,

$$K_r(T_m \rightarrow S_0) = \frac{16 \times 10^6 \pi^3 E(T_m)^3 \eta^2}{3h\epsilon_0} \left\{ \sum_n \langle T_m | H_{SOC} | S_n \rangle \langle S_n | M | S_0 \rangle \right\}^2$$  \hspace{1cm} (2)

where $E(T_m)$ is the energy of the $T_m \rightarrow S_0$ transition, $\langle T_m | H_{SOC} | S_n \rangle$ are the SOC matrix elements, $\langle S_n | M | S_0 \rangle$ the transition dipole moment between the nth singlet excited state ($S_n$) and the singlet ground state ($S_0$), and $\eta$ the refractive index of the medium. The term $M$ is related to the oscillator strength $f_n$ and the transition energy $E(S_n)$ of the ($S_n \rightarrow S_0$) transition via Equation (3)$^4,5$. 

\begin{align*}
\langle S_n | M | S_0 \rangle^2 &= \frac{3he^2}{8\pi m_e c E(S_n)} f_n
\end{align*}

Combining Equations (2) and (3) gives Equation (4),

\begin{equation}
K_r(T_m \rightarrow S_0) = \frac{\eta^2}{1.5} E(T_m)^3 \left( \sum_n \left( \frac{T_m | H_{SOC} | S_n}{E(S_n) - E(T_m)} \right) \frac{f_n}{E(S_n)} \right)^{1/2}
\end{equation}

The simple generalization of SOC operator for fine structure of the valence np-shell of the many electron atoms can be summarized as follows:

\begin{equation}
H_{SO} = \zeta \sum_l \vec{l}_i \vec{s}_i = \lambda \vec{L} \cdot \vec{S}
\end{equation}

where \( \vec{l}_i, \vec{s}_i \) are the single electron and the spin angular momentum operators, respectively (in \( \hbar \) units). Theoretical calculations provide \( \zeta 5d = 4860 \text{ cm}^{-1} \) for platinum metal. Then the one-center SOC element is evaluated by the coefficient of the natural atomic orbital of Pt 5d in the HOMO and HOMO-1 obtained from the natural bonding orbital (NBO) analysis.

**The non-radiative decay rate constant (\( K_m \))**

Based on the energy-gap law, the temperature-independent non-radiative decay rate constant from the \( T^m \) state to \( S^0 \) state can be simply expressed as below:

\begin{equation}
K_m(T_m \rightarrow S_0) \propto \exp \left\{ -\beta \left[ E(T_m) - E(S_0) \right] \right\}
\end{equation}

According to the kasha rule, \( m = 1 \) and \( \beta \) is a parameter related to the structural distortion between \( T_1 \) and \( S_0 \) states, and \( [E(T_m) - E(S_0)] \) is the energy gap between two corresponding states. It can be seen from Eqn (6) that the non-radiative decay rate is suppressed with small structural distortion and a large energy gap between the \( T^1 \) and \( S^0 \) states.

**Triplet exciton generation fractions (\( \chi_T \))**

The triplet exciton generation fractions (\( \chi_T \)) is calculated by the following formula:

\begin{equation}
\chi_T = 3 \sigma_T \left( \sigma_S + 3 \sigma_T \right) = 3 / (\sigma_S/\sigma_T + 3)
\end{equation}

where \( \sigma_S \) and \( \sigma_T \) represent the formation cross-sections of singlet and triplet excitons, respectively.
\[ R_{S/T} = \frac{\sigma_S}{\sigma_T} = \frac{(E_g - E_{S_\text{m} - T_m})}{(E_g - E_{S_0 - S_n})} \] (8)

where \( E_g \) is the energy gap between HOMO and LUMO, while \( E_{S_n - T_m} \) and \( E_{S_0 - S_n} \) are the excitation energies from the ground state \( (S_0) \) to the \( m^{\text{th}} \) excited triplet state and \( n^{\text{th}} \) excited singlet state, respectively \(^1,^7\).
Table S1. The xyz coordinates of the optimized structure of complex 1 considered in this work in two states of $S_0$ and $T_1$ at the DFT and TD-DFT/B3LYP level of theory.

| $S_0$ | $T_1$ |
|-------|-------|
| $\text{Pt}$ | $-0.60699$ | $0.59675$ | $1.93397$ | $1.90518$ | $15.07114$ | $15.06936$ |
| $\text{S}$ | $2.35335$ | $2.60417$ | $16.68072$ | $16.70250$ |
| $\text{N}$ | $-0.54976$ | $-0.12943$ | $15.73069$ | $15.72858$ |
| $\text{C}$ | $0.80348$ | $1.20476$ | $13.82792$ | $13.82034$ |
| $\text{C}$ | $1.51358$ | $1.89505$ | $12.82809$ | $12.83291$ |
| $\text{H}$ | $1.31643$ | $2.95506$ | $12.66589$ | $12.67777$ |
| $\text{C}$ | $2.46975$ | $1.25363$ | $12.03426$ | $12.00909$ |
| $\text{H}$ | $3.00261$ | $1.82145$ | $11.26609$ | $11.24803$ |
| $\text{C}$ | $2.74927$ | $-0.0621$ | $12.21489$ | $12.18932$ |
| $\text{H}$ | $3.49589$ | $-0.60764$ | $11.59494$ | $11.56860$ |
| $\text{C}$ | $2.06413$ | $-0.18119$ | $13.19628$ | $13.16780$ |
| $\text{H}$ | $2.28614$ | $-1.87925$ | $13.33279$ | $13.29883$ |
| $\text{C}$ | $1.10003$ | $-0.17894$ | $13.99870$ | $14.00210$ |
| $\text{C}$ | $0.35217$ | $-0.89128$ | $15.04445$ | $15.03472$ |
| $\text{C}$ | $0.50667$ | $-2.25230$ | $15.36289$ | $15.36406$ |
| $\text{H}$ | $1.22827$ | $-2.85652$ | $14.81399$ | $14.81870$ |
| $\text{C}$ | $-0.25674$ | $-2.82636$ | $16.37356$ | $16.38728$ |
| $\text{H}$ | $-0.13644$ | $-3.88380$ | $16.62031$ | $16.63445$ |
| $\text{C}$ | $-1.17594$ | $-2.03175$ | $17.06498$ | $17.07652$ |
| $\text{H}$ | $-1.79815$ | $-2.43470$ | $17.86526$ | $17.87738$ |
| $\text{C}$ | $-1.28439$ | $-0.69165$ | $16.70685$ | $16.72043$ |
| $\text{H}$ | $-1.98669$ | $-0.02930$ | $17.21645$ | $17.23276$ |
| $\text{C}$ | $-3.72027$ | $3.39011$ | $15.75261$ | $15.75386$ |
| $\text{H}$ | $-4.17432$ | $2.60318$ | $15.13463$ | $15.14331$ |
| $\text{C}$ | $-4.46244$ | $3.77970$ | $16.46711$ | $16.45739$ |
| $\text{H}$ | $-3.32675$ | $4.18706$ | $15.10652$ | $15.10023$ |
| $\text{C}$ | $-0.51568$ | $3.81729$ | $14.32432$ | $14.31885$ |
| $\text{C}$ | $-1.32428$ | $4.23699$ | $13.24504$ | $13.24416$ |
| $\text{C}$ | $0.36501$ | $4.78941$ | $14.84977$ | $14.84723$ |
| $\text{C}$ | $-1.26822$ | $5.54151$ | $12.73721$ | $12.74221$ |
| $\text{H}$ | $-2.00620$ | $3.52357$ | $12.77212$ | $12.76982$ |
| $\text{C}$ | $0.42123$ | $6.09310$ | $14.34178$ | $14.34373$ |
| $\text{H}$ | $1.04024$ | $4.51965$ | $15.66747$ | $15.66103$ |
| $\text{C}$ | $-0.39822$ | $6.49937$ | $13.27780$ | $13.28413$ |
| $\text{H}$ | $-1.91078$ | $5.81578$ | $11.89343$ | $11.90704$ |
| $\text{H}$ | $1.12741$ | $6.80797$ | $14.77839$ | $14.78034$ |
| $\text{C}$ | $-0.35513$ | $7.91449$ | $12.74869$ | $12.75950$ |
| $\text{H}$ | $-1.01288$ | $8.58641$ | $13.33036$ | $13.34530$ |
| $\text{H}$ | $0.66194$ | $8.33617$ | $13.80081$ | $13.81237$ |
| $\text{H}$ | $-0.68763$ | $7.96390$ | $11.69953$ | $11.71130$ |
| $\text{C}$ | $-1.74687$ | $4.04573$ | $17.63026$ | $17.63101$ |
| $\text{H}$ | $-0.91014$ | $3.68680$ | $18.24642$ | $18.25242$ |
| $\text{H}$ | $-1.39412$ | $4.82704$ | $16.94296$ | $16.93660$ |
| $\text{H}$ | $-2.55487$ | $4.41619$ | $18.27803$ | $18.27500$ |
**Table S2.** The xyz coordinates of the optimized structure of complex 2 considered in this work in two states of S₀ and T₁ at the DFT and TD-DFT/B3LYP level of theory.

|      | S₀         | T₀         |
|------|------------|------------|
|      | Pt 2.97548 | 3.71346    |
|      | C 0.38150  | 5.46825    |
|      | H 0.31822  | 4.84845    |
|      | C 0.58804  | 3.23019    |
|      | C 0.64405  | 7.03890    |
|      | C 0.77588  | 7.64859    |
|      | C -0.44207 | 7.28501    |
|      | H -1.15540 | 8.08307    |
|      | C -0.56115 | 6.49257    |
|      | H -1.36570 | 6.64377    |
|      | H 3.57246  | 0.41505    |
|      | C 2.08949  | -0.03070   |
|      | H 2.61761  | 0.40646    |
|      | C 1.16166  | -0.97128   |
|      | H 0.60727  | -1.42527   |
|      | H 0.24559  | 2.25504    |
|      | C -0.56970 | 2.17079    |
|      | H -0.11603 | 2.18876    |
|      | C -1.95804 | 2.07989    |
|      | C -2.55096 | 2.08592    |
|      | H -3.68577 | 2.02341    |
|      | C -1.74868 | 2.18243    |
|      | C -2.0523  | 2.19656    |
|      | C -0.35741 | 2.26429    |
|      | H 0.25537  | 2.34337    |
|      | C 2.77352  | 2.71303    |
|      | C 2.98352  | 1.74887    |
|      | C 2.73325  | 0.07090    |
|      | C 3.51705  | 2.11795    |
|      | H 3.67888  | 1.35683    |
|      | C 3.84237  | 3.45323    |
|      | C 4.25944  | 3.73936    |
|      | C 3.63926  | 4.41926    |

...
| $s_0$ | $t_1$ |
|-------|-------|
| H 3.89883 5.46352 -2.08971 | H 3.89883 5.46352 -2.08971 |
| C 3.11540 4.05151 -0.65838 | C 3.11540 4.05151 -0.65838 |
| H 2.97818 4.80556 0.12055 | H 2.97818 4.80556 0.12055 |

Table S3. The xyz coordinates of the optimized structure of complex 3 considered in this work in two states of $s_0$ and $t_1$ at the DFT and TD-DFT/B3LYP level of theory.
The xyz coordinates of the optimized structure of complex 4 considered in this work in two states of $S_0$ and $T_1$ at the DFT and TD-DFT/B3LYP level of theory.

| $S_0$  | $T_1$  |
|-------|-------|
| Pt    | 0.75740 11.93569 2.57741  | Pt    | 0.53534 11.81868 2.73966  |
| S     | 2.14786 10.09184 2.24789   | S     | 1.80207 9.85136 2.44111   |
| C     | 1.11413 8.65373 2.72933   | C     | 0.79197 8.72974 1.40200   |
| H     | 0.17249 8.65998 2.16412   | H     | 0.39225 9.25498 0.52655   |
| O     | 0.90834 8.75128 3.80336   | O     | -0.03628 8.38399 2.03542  |
| C     | 1.68509 7.73399 2.53492   | C     | 1.42187 7.87697 1.11142   |
| H     | 2.31855 9.75679 0.45675   | H     | 3.17312 10.26195 1.28983  |
| O     | 2.92538 8.84888 0.34107   | O     | 3.66607 9.32172 1.00261   |
| Pt    | 2.81808 10.63078 0.02293   | Pt    | 3.87065 10.88688 1.86264   |
| S     | 1.32527 9.63889 -0.00055  | S     | 2.78561 10.82203 0.42766   |
| C     | -0.01113 11.88702 0.58283  | C     | -0.31443 11.65517 0.81083  |
| O     | 0.64931 12.36885 -0.41775  | O     | 0.25224 11.88554 -0.32661  |
| C     | 1.80674 12.75509 -0.49702  | C     | 1.41884 12.14524 -0.58208  |
| C     | -0.23546 12.38600 -1.69309  | C     | -0.77310 11.74056 -1.48186 |
| F     | -0.54920 11.12640 -2.07396  | F     | -1.11805 10.43419 -1.62510 |
| F     | -1.40568 13.04271 -1.47512  | F     | -1.90860 12.43201 -1.23814 |
| F     | 0.37168 12.98610 -2.72664  | F     | -0.28227 12.16115 -2.65405 |
| C     | 1.26206 12.17296 4.50249   | C     | 1.16984 12.18182 4.58330   |
| C     | 2.19647 11.45724 5.20704   | C     | 2.08389 11.41695 5.34554   |
| H     | 2.76920 10.64352 4.81851   | H     | 2.51819 10.51363 4.91135   |
| C     | 2.43568 11.77043 6.61361   | C     | 2.47909 11.77573 6.69320   |
| H     | 3.16909 11.19081 7.18099   | H     | 3.19067 11.15056 7.23366   |
| C     | 1.75003 12.82160 7.23279   | C     | 1.94851 12.91463 7.24440   |
| H     | 1.93943 13.06656 8.28006   | H     | 2.22566 13.22477 8.25491   |
| O     | 0.82512 13.56006 6.49656   | O     | 1.01803 13.71784 6.51011   |
| C     | -1.16459 15.07009 4.71561  | C     | -0.99069 15.28505 4.70610  |
| C     | -2.03653 15.66758 8.30008  | C     | -1.88042 15.85654 3.82190  |
| H     | -2.65362 16.51363 4.12094  | H     | -2.40434 16.77722 4.08702  |
| C     | -2.11608 15.17193 2.50517  | C     | -2.11148 15.23605 2.56247  |
| H     | -2.78927 15.60522 1.76473  | H     | -2.81197 15.65041 1.83804  |
| C     | -1.30888 14.09595 2.15199  | C     | -1.41963 14.07357 2.25901  |
Table S5. The xyz coordinates of the optimized structure of complex 5 considered in this work in two states of $S_0$ and $T_1$ at the DFT and TD-DFT/B3LYP level of theory.

|          | $S_0$          | $T_1$          |
|----------|----------------|----------------|
| Pt       | -0.75902       | -0.77934       |
| S        | -2.48160       | -2.73633       |
| N        | -0.52906       | -0.44162       |
| C        | 0.65855        | 0.48876        |
| C        | 1.28329        | 0.90994        |
| H        | 1.00662        | 0.41485        |
| C        | 2.25721        | 1.96016        |
| H        | 2.72016        | 2.28116        |
| H        | 2.64352        | 2.61285        |
| H        | 3.40422        | 3.44995        |
| C        | 2.04547        | 2.19927        |
| C        | 2.34975        | 2.72704        |
| C        | 1.06366        | 1.10282        |
| C        | 0.40523        | 0.51899        |
| C        | 0.67224        | 0.78430        |
| H        | 1.41976        | 1.52044        |
| C        | -0.01330       | 0.10249        |
| H        | 0.19410        | 0.31075        |
| C        | -0.96771       | -0.89228       |
| H        | -1.53278       | -1.45841       |
| C        | -1.18763       | -1.12304       |
| C        | -1.92198       | -1.87493       |
| C        | -3.92796       | -3.85575       |
| H        | -4.34226       | -4.25720       |
| H        | -4.67609       | -4.67715       |
| H        | -3.61684       | -3.30614       |
| C        | -1.93963       | -2.17772       |
| H        | -1.06253       | -1.45957       |
| H        | -1.65708       | -1.68446       |
| H        | -2.74651       | -3.04158       |
| C        | -0.80147       | -0.53576       |
| H        | -1.09147       | -1.24141       |
| H        | -1.50456       | -0.76677       |
Table S6. Frontier molecular orbital compositions (%) in the ground state for complexes 2-5.

| Complex | Pt  | ppy   | Me   | P(Ph)₂(C₃H₅) |
|---------|-----|-------|------|--------------|
| 2       |     |       |      |              |
| HOMO-5  | 71  | 8     | 10   | 11           |
| HOMO-4  | 13  | 28    | 57   |              |
| HOMO-3  | 13  | 86    | -    |              |
| HOMO-2  | 74  | 19    | 1    |              |
| HOMO-1  | 81  | 13    | 1    |              |
| HOMO    | 42  | 55    | 2    |              |
| LUMO    | 7   | 90    | 1    |              |
| LUMO+1  | 2   | 24    |      |              |
| LUMO+2  | 2   | 55    |      |              |
| LUMO+3  | 2   | 8     |      |              |
| LUMO+4  | 2   | 16    |      |              |
| LUMO+5  | 1   | 2     |      |              |

| Complex | Pt  | ppy   | Spy  | PPh₃ |
|---------|-----|-------|------|------|
| 3       |     |       |      |      |
| HOMO-5  | 33  | 47    | 1    |      |
| HOMO-4  | 30  | 32    | 36   |      |
| HOMO-3  | 6   | 25    | 68   |      |
| HOMO-2  | 70  | 12    | 15   |      |
| HOMO-1  | 33  | 65    | 1    |      |
| HOMO    | 8   | 4     | 87   |      |
| LUMO    | 7   | 91    | 1    |      |
| LUMO+1  | 1   | 78    |      |      |
| LUMO+2  | 1   | 20    |      |      |
| LUMO+3  | 3   | 16    |      |      |
| LUMO+4  | 1   | 8     |      |      |
| LUMO+5  | 3   | 9     |      |      |
| LUMO+6  | 1   | 1     |      |      |

| Complex | Pt  | ppy   | S(Me)₂ | CO₂CF₃ |
|---------|-----|-------|--------|--------|
| 4       |     |       |        |        |
| HOMO-5  | 56  | 15    | 5      | 24     |
| HOMO-4  | 24  | 5     | 6      | 30     |
| HOMO-3  | 42  | 22    | 3      | 4      |
| HOMO-2  | 18  | 75    | 5      | 3      |
| HOMO-1  | 73  | 5     | 15     | 4      |
| HOMO    | 37  | 59    | 5      | 4      |
| LUMO    | 6   | 92    | 2      | 2      |
| LUMO+1  | 1   | 99    | -      | -      |
| LUMO+2  | 50  | 27    | 18     | 5      |
| LUMO+3  | 16  | 74    | 9      | 1      |
| LUMO+4  | 6   | 36    | 54     | 4      |
| LUMO+5  | 4   | 22    | 17     | 57     |

| Complex | Pt  | ppy   | S(Me)₂ | Me   |
|---------|-----|-------|--------|------|
| 5       |     |       |        |      |
| HOMO-5  | 17  | 30    | 38     | 15   |
| HOMO-4  | 76  | 7     | 9      | 8    |
| HOMO-3  | 9   | 91    | -      | -    |
| HOMO-2  | 77  | 16    | -      | -    |
| HOMO-1  | 90  | 5     | -      | -    |
| HOMO    | 39  | 59    | 2      | -    |
| LUMO    | 7   | 91    | 1      | -    |
| LUMO+1  | 1   | 99    | -      | -    |
| LUMO+2  | 21  | 44    | 35     | -    |
| LUMO+3  | 5   | 55    | 40     | -    |
| LUMO+4  | 2   | 97    | 1      | -    |
| LUMO+5  | 37  | 32    | 20     | 11   |
Table S7. The vertical absorption properties of complex 2-5.

| Complex/State | Major contribution | $f$   | E(eV)  | $\lambda_{cal}$(nm) | assignment       |
|---------------|--------------------|-------|--------|----------------------|------------------|
| 2 S$_1$       | H-1 $\rightarrow$ L (55.3%) | 0.0052 | 3.233  | 383.49               | $^1$MLCT/ILCT   |
|               | H $\rightarrow$ L (43.5%)     |       |        |                      |                  |
| S$_2$         | H $\rightarrow$ L (50.7%)     | 0.0126 | 3.277  | 378.40               | $^1$MLCT/ILCT   |
|               | H-1 $\rightarrow$ L (43.0%)   |       |        |                      |                  |
| S$_3$         | H-2 $\rightarrow$ L (86.1%)   | 0.0690 | 3.659  | 338.84               | $^1$MLCT/ILCT/LLCT|
|               | H $\rightarrow$ L+2 (3.5%)    |       |        |                      |                  |
|               | H $\rightarrow$ L (2.7%)      |       |        |                      |                  |
| S$_4$         | H-1 $\rightarrow$ L+1 (57.1%) | 0.0012 | 3.282  | 323.92               | $^1$MLCT/LLCT   |
|               | H $\rightarrow$ L+1 (28.8%)   |       |        |                      |                  |
|               | H $\rightarrow$ L+2 (5.1%)    |       |        |                      |                  |
| S$_5$         | H $\rightarrow$ L+1 (27.2%)   | 0.0265 | 3.874  | 320.02               | $^1$MLCT/LLCT   |
|               | H-1 $\rightarrow$ L+1 (22.1%) |       |        |                      |                  |
|               | H-1 $\rightarrow$ L+2 (19.3%) |       |        |                      |                  |
|               | H-3 $\rightarrow$ L (9.9%)    |       |        |                      |                  |
|               | H-2 $\rightarrow$ L (3.0%)    |       |        |                      |                  |
| S$_6$         | H-1 $\rightarrow$ L+2 (53.9%) | 0.0165 | 3.887  | 318.97               | $^1$MLCT/ILCT   |
|               | H $\rightarrow$ L+2 (28.8%)   |       |        |                      |                  |
|               | H-1 $\rightarrow$ L+1 (7.7%)  |       |        |                      |                  |
| S$_7$         | H $\rightarrow$ L+2 (32.9%)   | 0.0003 | 3.941  | 314.57               | $^1$MLCT/ILCT/LLCT|
|               | H $\rightarrow$ L+1 (31.6%)   |       |        |                      |                  |
|               | H-1 $\rightarrow$ L+2 (17.2%) |       |        |                      |                  |
|               | H-1 $\rightarrow$ L+1 (7.1%)  |       |        |                      |                  |
|               | H-3 $\rightarrow$ L (3.6%)    |       |        |                      |                  |
| S$_8$         | H-1 $\rightarrow$ L+3 (72.1%) | 0.0030 | 4.017  | 308.68               | $^1$MLCT/LLCT   |
|               | H $\rightarrow$ L+3 (22.3%)   |       |        |                      |                  |
| S$_9$         | H $\rightarrow$ L+3 (50.9%)   | 0.0053 | 4.086  | 303.47               | $^1$MLCT/LLCT   |
|               | H-1 $\rightarrow$ L+3 (21.0%) |       |        |                      |                  |
|               | H-3 $\rightarrow$ L (8.0%)    |       |        |                      |                  |
|               | H $\rightarrow$ L+2 (5.7%)    |       |        |                      |                  |
|               | H $\rightarrow$ L+1 (4.4%)    |       |        |                      |                  |
|               | H-1 $\rightarrow$ L+2 (1.6%)  |       |        |                      |                  |
| S$_{10}$      | H-5 $\rightarrow$ L (76.6%)   | 0.0043 | 4.096  | 302.68               | $^1$MLCT/LLCT   |
|               | H-4 $\rightarrow$ L (11.8%)   |       |        |                      |                  |
|               | H-3 $\rightarrow$ L+2 (2.9%)  |       |        |                      |                  |
| Complex/State | Major contribution (%) | $f$ | E(eV) | $\lambda_{cal}$(nm) | assignment |
|--------------|------------------------|-----|-------|---------------------|------------|
| S1           | H $\rightarrow$ L (99.0%) | 0.0023 | 2.293 | 540.61 | $^1$LLCT |
| S2           | H $\rightarrow$ L+1 (76.8%) | 0.0007 | 2.975 | 416.720 | $^1$MLCT/$^1$LLCT |
|              | H $\rightarrow$ L+3 (11.2%) |       |       |        |            |
|              | H $\rightarrow$ L+2 (9.2%) |       |       |        |            |
| S3           | H $\rightarrow$ L+3 (61.3%) | 0.0050 | 3.038 | 408.090 | $^1$MLCT/$^1$LLCT |
|              | H $\rightarrow$ L+2 (28.8%) |       |       |        |            |
| S4           | H $\rightarrow$ L+2 (60.7%) | 0.0007 | 3.096 | 400.420 | $^1$MLCT/$^1$LLCT |
|              | H $\rightarrow$ L+1 (20.0%) |       |       |        |            |
|              | H $\rightarrow$ L+3 (18.1%) |       |       |        |            |
| S5           | H-1 $\rightarrow$ L (95.5%) | 0.0363 | 3.284 | 377.540 | $^1$MLCT/$^1$ILCT |
| S6           | H $\rightarrow$ L+4 (93.8%) | 0.0042 | 3.384 | 366.340 | $^1$MLCT/$^1$LLCT |
| S7           | H-2 $\rightarrow$ L (96.1%) | 0.0024 | 3.435 | 360.990 | $^1$MLCT/$^1$LLCT |
| S8           | H-4 $\rightarrow$ L (95.5%) | 0.0050 | 3.598 | 344.600 | $^1$MLCT/$^1$ILCT/$^1$LLCT |
| S9           | H $\rightarrow$ L+5 (91.7%) | 0.0037 | 3.608 | 343.630 | $^1$MLCT/$^1$LLCT |
| S10          | H $\rightarrow$ L+6 (92.7%) | 0.0020 | 3.721 | 333.200 | $^1$MLCT/$^1$LLCT |

| Complex/State | Major contribution (%) | $f$ | E(eV) | $\lambda_{cal}$(nm) | assignment |
|--------------|------------------------|-----|-------|---------------------|------------|
| S1           | H $\rightarrow$ L (96.6%) | 0.0240 | 3.171 | 391.03 | $^1$MLCT/$^1$ILCT/$^1$LLCT |
| S2           | H-1 $\rightarrow$ L (96.0%) | 0.0054 | 3.458 | 358.490 | $^1$MLCT/$^1$LLCT |
| S3           | H $\rightarrow$ L+1 (85.2%) | 0.0067 | 3.870 | 320.340 | $^1$MLCT/$^1$ILCT/$^1$LLCT |
|              | H-3 $\rightarrow$ L (9.8%) |       |       |        |            |
| S4           | H-2 $\rightarrow$ L (55.4%) | 0.0384 | 3.930 | 315.500 | $^1$MLCT/$^1$ILCT/$^1$LLCT |
|              | H-3 $\rightarrow$ L (31.9%) |       |       |        |            |
|              | H-4 $\rightarrow$ L (4.0%) |       |       |        |            |
| S5           | H-2 $\rightarrow$ L (27.7%) | 0.0503 | 4.103 | 302.210 | $^1$MLCT/$^1$ILCT/$^1$LLCT |
|              | H-3 $\rightarrow$ L (25.1%) |       |       |        |            |
|              | H-5 $\rightarrow$ L (16.6%) |       |       |        |            |
|              | H $\rightarrow$ L+2 (12.6%) |       |       |        |            |
|              | H-4 $\rightarrow$ L (4.8%) |       |       |        |            |
|              | H $\rightarrow$ L+1 (4.1%) |       |       |        |            |
| S6           | H-2 $\rightarrow$ L (76.6%) | 0.0096 | 4.157 | 298.230 | $^1$MLCT/$^1$ILCT |
|              | H-3 $\rightarrow$ L (8.2%) |       |       |        |            |
|              | H-1 $\rightarrow$ L+2 (2.4%) |       |       |        |            |
| S7           | H-1 $\rightarrow$ L+1 (96.8%) | 0.0002 | 4.198 | 295.310 | $^1$MLCT/$^1$LLCT |
| S8           | H-4 $\rightarrow$ L (61.8%) | 0.0323 | 4.242 | 292.260 | $^1$MLCT/$^1$ILCT/$^1$LLCT |
|              | H-3 $\rightarrow$ L (16.3%) |       |       |        |            |
|              | H-5 $\rightarrow$ L (12.1%) |       |       |        |            |
| S9           | H-5 $\rightarrow$ L (42.5%) | 0.0740 | 4.317 | 287.190 | $^1$MLCT/$^1$ILCT/$^1$LLCT |
|              | H-3 $\rightarrow$ L (19.1%) |       |       |        |            |
|              | H-2 $\rightarrow$ L+1 (12.5%) |       |       |        |            |
|              | H-1 $\rightarrow$ L+2 (12.0%) |       |       |        |            |
|              | H-2 $\rightarrow$ L (4.0%) |       |       |        |            |
| Complex/State | Major contribution (%) | f   | E(eV) | λcal(nm) | assignment         |
|---------------|------------------------|-----|-------|----------|--------------------|
| S_10          | H-1 → L+2 (70.3%)      | 0.0178 | 4.337 | 285.860 | ^1MLCT/^LLCT       |
|               | H-5 → L (11.5%)        |      |       |          |                    |
|               | H-4 → L (4.3%)         |      |       |          |                    |
|               | H-4 → L+2 (3.6%)       |      |       |          |                    |
|               | H-3 → L+2 (2.5%)       |      |       |          |                    |

| Complex/State | Major contribution (%) | f   | E(eV) | λcal(nm) | assignment         |
|---------------|------------------------|-----|-------|----------|--------------------|
| S_5           | H-1 → L (98.9%)        | 0.0043 | 3.162 | 392.07   | ^1MLCT/^LLCT       |
| S_2           | H → L (91.5%)          | 0.0139 | 3.188 | 388.870  | ^1MLCT/^ILCT       |
| S_3           | H-2 → L (86.1%)        | 0.0599 | 3.564 | 347.880  | ^1MLCT/^LLCT       |
|               | H → L+1 (4.6%)         |      |       |          |                    |
| S_4           | H-1 → L+1 (99.2%)      | 0.0001 | 3.778 | 328.140  | ^1MLCT/^LLCT       |
| S_5           | H → L+1 (84.2%)        | 0.0350 | 3.806 | 325.750  | ^1MLCT/^ILCT       |
|               | H → L (8.7%)           |      |       |          |                    |
| S_6           | H-4 → L (98.4%)        | 0.0001 | 3.874 | 320.010  | ^1MLCT/^LLCT       |
| S_7           | H-2 → L+1 (69.0%)      | 0.0166 | 4.030 | 307.630  | ^1MLCT/^ILCT/^LLCT |
|               | H-3 → L (22.8%)        |      |       |          |                    |
| S_8           | H-3 → L (53.6%)        | 0.1915 | 4.262 | 290.920  | ^1MLCT/^ILCT/^LLCT |
|               | H-2 → L+1 (25.1%)      |      |       |          |                    |
|               | H → L+2 (8.2%)         |      |       |          |                    |
|               | H-3 → L+1 (4.6%)       |      |       |          |                    |
| S_9           | H-5 → L (96.4%)        | 0.0003 | 4.429 | 279.960  | ^1MLCT/^LLCT       |
| S_10          | H-4 → L+1 (98.9%)      | 0.0001 | 4.533 | 273.520  | ^1MLCT/^LLCT       |
Figure S1. Absorption spectra of Complex 2 at their optimized S₀ geometry in gas phase and in Cl₂CH₂ solution with its experimental spectra.
Complex 3:

![Graph showing oscillator strength against wavelength in nm. The graph includes data from calculations in CH₂Cl₂ and gas phase, as well as experimental data in CH₂Cl₂.]
Complex 4:

- Calculated in Cl₂CH₂
- Calculated in gas phase
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