Theoretical studies on the photophysical properties of luminescent pincer gold(III) arylacetylide complexes: the role of \(\pi\)-conjugation at the C-deprotonated \([C^N^C]\) ligand\(^\dagger\)

Glenna So Ming Tong, *a Kaai Tung Chan, a Xiaoyong Chang a and Chi-Ming Che*ab

We have performed theoretical analyses of the photophysical properties of a series of cyclometalated gold(III) arylacetylide complexes, \([C^N^C]\)Au\(\text{II}[C\equiv\text{CPh}-4-\text{OMe}]\), with different extents of \(\pi\)-conjugation at the doubly C-deprotonated \([C^N^C]\) ligand via replacement of one of the phenyl moieties in the non-conjugated \(C^N^C\) ligand (1) by a naphthalenyl (2) or a fluorenyl moiety (3-exo and 3-endo; HCH\(\equiv\)N\(\equiv\)CH = 2,6-diphenylpyridine). Conforming to the conventional wisdom that extended \(\pi\)-conjugation imposes rigidity on the structure of the 3IL\((\pi\pi^\ast(C^N^C))\) excited state (IL = intraligand), the calculated Huang–Rhys factors for the 3IL \(\rightarrow S_0\) transition follow the order: 1 \(>\) 2 \(>\) 3-exo \(\sim\) 3-endo, which corroborates qualitatively the experimental non-radiative decay rate constants, \(k_{nr}\): 1 \(\gg\) 2 \(>\) 3-exo, but not 3-endo. Density Functional Theory (DFT) calculations revealed that there is an additional triplet excited state minimum of 3LLCT character \((LLCT = \text{ligand-to-ligand charge transfer};\; 3[\pi(C\equiv\text{CPh}-4-\text{OMe}) \rightarrow \pi^\ast(C^N^C)])\) for complexes 1 and 3-endo. This 3LLCT excited state, possessing a large out-of-plane torsional motion between the planes of the \(C^N^C\) and arylacetylide ligands, has a double minimum anharmonic potential energy surface along this torsional coordinate which leads to enhanced Franck–Condon overlap between the 3LLCT excited state and the ground state. Together with the larger spin–orbit coupling (SOC) and solvent reorganization energy for the 3LLCT \(\rightarrow S_0\) transition compared with those for the 3IL \(\rightarrow S_0\) transition, the calculated \(k_{nr}\) values for the 3LLCT \(\rightarrow S_0\) transition are more than 690- and 1500-fold greater than the corresponding 3IL \(\rightarrow S_0\) transition for complexes 1 and 3-endo respectively. Importantly, when this 3LLCT \(\rightarrow S_0\) decay channel is taken into consideration, the non-radiative decay rate constant \(k_{nr}\) could be reproduced quantitatively and in the order of: 1 \(\gg\) 3-endo, 2 \(>\) 3-exo. This challenges the common view that the facile non-radiative decay rate of transition metal complexes is due to the presence of a low-lying metal-centred 3dd or 3LMCT excited state \((\text{LMCT = ligand-to-metal charge transfer})\). By analysis of the relative order of MOs of the chromophoric \([C^N^C]\) cyclometalated and arylacetylide ligands, one may discern why complexes 1 and 3-endo have a low-lying 3LLCT excited state while 3-exo does not.

**Introduction**

Gold(III) complexes are being actively studied as potential anticancer drugs\(^1\) and catalysts.\(^2\)\(^3\) However, the study of the spectroscopic and luminescent properties of gold(III) complexes is still in its infancy, in particular when compared to their isoelectronic platinum(II) counterparts, which are known to display rich photophysical behaviours. One of the impediments to the progress of photoluminescence of gold(III) complexes is the high electropolylicity of the gold(III) ion and the presence of a low-lying Au(5d\(\pi^\ast\)) orbital. In effect, the deactivating ligand-to-metal charge transfer \((\text{LMCT})\) and/or dd ligand-field excited states become close in energy to the emitting excited state, leading to efficient luminescence quenching in gold(III) complexes.\(^4\) To circumvent this problem, Yam and co-workers have coupled various strong \(\sigma\)-donating ligands, such as arylacetylide and \(N\)-heterocyclic carbenes (NHC), to the gold(III) cyclometalated complexes;
these complexes were reported to be weakly emissive in solution ($\phi < 0.01$) at room temperature.\(^7\)

To enhance the emission quantum yield, the structural distortion between the emitting excited state and the ground state must be minimized, thereby decreasing the non-radiative decay rate.\(^6\) This can be achieved by designing emitting molecules with highly rigid ligand scaffolds, for example, by extended $\pi$-conjugation at the cyclometalated ligand\(^7\) (see Table 1 for a comparison between the emission quantum yields of selected examples of gold(III) cyclometalated complexes with different extents of $\pi$-conjugation at the [C$^\text{N}$C$^\text{N}$C] ligand).\(^{3a,5a}\) A particularly striking example is the series of gold(III) complexes with a fluorenly moiety incorporated into the doubly deprotonated [C$^\text{N}$C$^\text{N}$C] ligand.\(^7\) In this case, the room temperature emission quantum yields of the gold(III) cyclometalated complexes in solution reach 0.58, and the corresponding non-radiative decay rate constant ($k_{nr}$) falls to $1.74 \times 10^3$ s$^{-1}$ (Table 1, column 5). In other words, $k_{nr}$ drops more than four orders of magnitude when one of the phenyl moieties in the non-conjugated C$_{11}$N$^\text{C}$N$^\text{C}$ ligand (Table 1, column 2; HCN$_2$N$^\text{C}$CH = 2,6-diphenylpyrididine) is replaced by a fluorenly moiety.\(^7\) Similar enhancement in emission quantum yield has also been reported for fluorene-functionalized cyclometalated platinum(II) complexes when compared with the non-conjugated C$_{11}$N$^\text{C}$N$^\text{C}$ analogue;\(^6\) the enhanced luminescence is attributed to the rigid $\pi$-conjugated fluorene unit which minimizes structural distortion between the emitting triplet excited state and the ground state.

Interestingly, when the fluorenly moiety is disposed in such a fashion that the long alkyl chains are “endo” in the gold(III) pincer complex (last column in Table 1), there is a dramatic decrease in emission quantum yield ($\phi \sim 0.02$, $\tau \sim 14.5$ µs) and a nearly 40-fold increase in the non-radiative decay rate constant ($k_{nr} \sim 6.76 \times 10^4$ s$^{-1}$) when compared with its “exo” analogue (Table 1, column 5; see ESI† for the synthetic procedure and photophysical properties of the “endo” complex). This means that, even with a seemingly suitable cyclometalated ligand (i.e., a strong $\sigma$-donor which raises the energy of the dd or LMCT excited state and a cyclometalated ligand with extended $\pi$-conjugation that minimizes structural distortion), the phosphorescence efficiency of gold(III) complexes is not necessarily high. Thus, for effective design of functional luminescent molecules, it is important to understand the effect of $\pi$-conjugation in the C-deprotonated cyclometalated [C$^\text{N}$C$^\text{N}$C] ligand on the excited state properties of these luminescent gold(III) complexes.

In this work, we have performed a detailed theoretical analysis of four gold(III) complexes with different [C$^\text{N}$C$^\text{N}$C] cyclometalated ligand scaffolds (Chart 1), namely, the non-conjugated C$_{11}$N$^\text{C}$N$^\text{C}$ (I) and the $\pi$-conjugated C$_{3}$N$^\text{C}$N$^\text{C}$ (2) and C$^\text{N}$C$_{3}$N$^\text{C}$ (3-endo and 3-exo); complexes 2 and 3-exo (and 3-endo) have one of the phenyl moieties of 1 replaced by a naphthalenyl (np) or a fluorenly (fl) moiety respectively. The ancillary ligand, $p$-methoxyphenyl acetylide ([C=CPh-4-OMe]$^-$) is kept the same for all four complexes. A detailed list of definitions and abbreviations is provided in the appendix.

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**Table 1** Photophysical properties of gold(III) pincer-type complexes in dichloromethane solution at room temperature. For R = C≡CPh-4-OMe, $n = 0$ and for R = 1,3-dimethylimidazol-2-ylidene, $n = 1$. C$_{3}$N$^\text{C}$N$^\text{C}$ = pincer-type cyclometalated ligand; X = H, np, or fl.

<table>
<thead>
<tr>
<th>Complex</th>
<th>$\phi$</th>
<th>$\tau$</th>
<th>$k_{nr}$</th>
<th>Complex</th>
<th>$\phi$</th>
<th>$\tau$</th>
<th>$k_{nr}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Au$^{III}$(C$_{11}$N$^\text{C}$N$^\text{C}$)R]$^a$</td>
<td>$0.0004$</td>
<td>$0.017 \mu$s$^{a,b}$</td>
<td>$5.88 \times 10^2$ s$^{-1}$</td>
<td>[Au$^{III}$(C$_{3}$N$^\text{C}$N$^\text{C}$)R]$^a$</td>
<td>$0.09$</td>
<td>$25 \mu$s$^{a}$</td>
<td>$3.64 \times 10^4$ s$^{-1}$</td>
</tr>
<tr>
<td>[Au$^{III}$(C$<em>{3}$N$^\text{C}$N$^\text{C}$)$</em>{np}$R]$^a$</td>
<td>$0.08$</td>
<td>$64 \mu$s$^{a}$</td>
<td>$1.44 \times 10^3$ s$^{-1}$</td>
<td>[Au$^{III}$(C$<em>{3}$N$^\text{C}$N$^\text{C}$)$</em>{fl}$R]$^a$</td>
<td>$0.58$</td>
<td>$242 \mu$s$^{a}$</td>
<td>$1.74 \times 10^4$ s$^{-1}$</td>
</tr>
<tr>
<td>[Au$^{III}$(C$<em>{3}$N$^\text{C}$N$^\text{C}$)$</em>{fl}$R]$^a$</td>
<td>$0.02$</td>
<td>$14.5$ µs (this work)</td>
<td>$6.76 \times 10^4$ s$^{-1}$</td>
<td>[exo-[Au$^{III}$(C$_{3}$N$^\text{C}$N$^\text{C}$)R]$^a$</td>
<td>$0.039$</td>
<td>$0.6 \mu$s$^{a}$</td>
<td>$3.35 \times 10^3$ s$^{-1}$</td>
</tr>
<tr>
<td>[endo-[Au$^{III}$(C$_{3}$N$^\text{C}$N$^\text{C}$)R]$^a$</td>
<td>$0.055$</td>
<td>$282 \mu$s$^{a}$</td>
<td>$3.53 \times 10^3$ s$^{-1}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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\(^{a}\)Reference 3a, \(^{b}\)Reference 5a, \(^{c}\)Reference 3a, \(^{d}\)Reference 1.

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Theoretical background

Dynamical solvent effect on excited state and ground state energies

Density Functional Theory (DFT) and time-dependent DFT (TDDFT) are the commonly used tools to study the ground state and excited state properties of medium- to large-sized molecules. In the literature, computation of emission energies in solutions is performed using either linear response TDDFT (LR-TDDFT) or the ΔSCF method. For both types of calculations, both the excited state of interest and the ground state are calculated with equilibrium (EQ) solvation. However, in an emission process, the ground state should be treated with solvent polarization in the non-equilibrium (NEQ) regime because the time scale of an emission process is much faster than that of the solvent dynamics. Therefore, for a rigorous consideration of the solvent effect on an emission process, the ground state should be computed with non-equilibrium solvation, i.e., only the solvent electronic polarization (the “fast” component) is in equilibrium with the ground state electron density of the solute, while the solvent nuclear polarization (the “slow” component) remains equilibrated with the excited state electron density of the solute. For this reason, we have employed the state-specific (SS) approach to account for the dynamical solvent effect. Within the SS scheme, rather than using the ground state electronic density as in LR-TDDFT and ΔSCF, the electronic density of the emitting excited state is used to compute the ground state energy.\(^\text{10}\) Therefore, the emission energy within the SS scheme (\(\Delta E_{\text{em}}^{\text{SS}}\)) is given by:

\[
\Delta E_{\text{em}}^{\text{SS}} = E_{\text{EQ}}^{\text{ES}}(Q_0^{\text{ES}}) - E_{\text{NEQ}}^{\text{G}}(Q_0^{\text{G}})
\]

\(E_{\text{EQ}}^{\text{ES}}(Q_0^{\text{ES}})\) is the energy of the excited state (ES) with equilibrium solvation at the optimized excited state geometry (\(Q_0^{\text{ES}}\)), and \(E_{\text{NEQ}}^{\text{G}}(Q_0^{\text{G}})\) is the energy of the ground state (GS) with non-equilibrium solvation at \(Q_0^{\text{G}}\) (Fig. 1).\(^\text{11}\)

The SS approach also allows one to estimate the solvent reorganization energy \(\lambda_s\), which is the ground state energy difference calculated with non-equilibrium solvation \((E_{\text{EQ}}^{\text{SS}}(Q_0^{\text{ES}}))\) and with equilibrium solvation \((E_{\text{EQ}}^{\text{G}}(Q_0^{\text{ES}}))\) at the optimized excited state geometry \(Q_0^{\text{ES}}\) (Fig. 1):

\[
\lambda_s = E_{\text{NEQ}}^{\text{SS}}(Q_0^{\text{ES}}) - E_{\text{EQ}}^{\text{G}}(Q_0^{\text{ES}})
\]

Similarly, the intramolecular reorganization energy computed within the SS approach \(\lambda_v^{\text{SS}}\) is given by:

\[
\lambda_v^{\text{SS}} = E_{\text{EQ}}^{\text{SS}}(Q_0^{\text{ES}}) - E_{\text{EQ}}^{\text{G}}(Q_0^{\text{ES}})
\]

where \(E_{\text{EQ}}^{\text{SS}}(Q_0^{\text{ES}})\) is the energy of the ground state computed with equilibrium solvation at the optimized ground state geometry \(Q_0^{\text{G}}\) (Fig. 1).

Radiative decay rate constant \((k_i)\)

The total radiative decay rate constant from the vibrational ground state of the emitting \(T_1\) \(\alpha\)-spin sub-state \((k_i^{\alpha})\) to the \(S_0\) state vibrational manifolds is given by the sum of individual radiative decay rate constants (denoted \(k_i^{\alpha}(\bar{v})\), each corresponding to a single vibronic transition, \(T_1^{\alpha}(\bar{v} = 0) \rightarrow S_0(\bar{v}')\), with photon energy, \(\bar{v}\), and vibrational quantum number for the \(T_1\) and \(S_0\) states, \(\bar{v}'\) and \(\bar{v}'\), respectively:

\[
k_i^{\alpha}(T_1 \rightarrow S_0) = \sum_{\bar{v}} k_i^{\alpha}(\bar{v})
\]

The radiative decay rate constant for the single vibronic transition can be calculated from the Einstein coefficient of spontaneous emission:

\[
k_i^{\alpha}(\bar{v}) = \frac{8\pi^2 \eta^3 |\mathbf{M}_i^{\alpha}(Q)|^2}{3\varepsilon_0 h}
\]

where \(\eta\) is the solvent refractive index, \(\bar{v}\) is the triplet emission energy (in cm\(^{-1}\)), and \(\mathbf{M}_i^{\alpha}(Q)\) is the transition dipole moment of the \(T_1^{\alpha}\rightarrow S_0\) transition (in e\(\alpha_0\)), and the prefactor \(8\pi^2/3\varepsilon_0 h = 2.0261 \times 10^{-6}\).

By invoking the Condon approximation \((i.e., \mathbf{M}_i^{\alpha}(Q) \approx \mathbf{M}_i^{\alpha}(Q_0^{T_1}))\) with \(Q_0^{T_1}\) being the optimized \(T_1\) excited state geometry) and combining eqn (4) and (5), the total radiative decay rate constant, \(k_i^{\alpha}\), is given by:

\[
k_i^{\alpha}(T_1 \rightarrow S_0) = \frac{8\pi^2 \eta^3 |\mathbf{M}_i^{\alpha}(Q_0^{T_1})|^2}{3\varepsilon_0 h} \sum_{\bar{v}} \left| \int \chi_{\bar{v}}(\bar{v}) \chi_{\bar{v}'}(\bar{v}') \text{d}Q \right|^2
\]

\(\chi_{\bar{v}}\) and \(\chi_{\bar{v}'}\) are the vibrational wavefunctions of the \(S_0\) and the \(T_1\) states respectively.

Unless the emission spectrum is sharply peaked, as in an atomic emission spectrum, one should not take the integral in eqn (6) as unity and replace the summation in eqn (6) by the emission peak maximum, \(\bar{v}_{\text{max}}\); such an approximation is justified only if the molecule has fixed nuclei. In reality, however, the nuclei are in motion, bringing about a broadening of the emission spectrum. These nuclear motions \((i.e.,\ vibrations)\) can be accounted for by the Franck–Condon factors.
computational simulation. The total radiative decay rate constant \( k_{sr} \) can be obtained either from experiment or by application of Fermi’s Golden Rule expression, assuming that both electronic and nuclear degrees of freedom are harmonic:

\[
\frac{8\pi^{2}\eta^{3}}{3\epsilon_{0}\hbar} |\mathbf{T}^{\text{eff}}(Q_{0}^{\text{T}})|^{2}
\]

with \( I(\tilde{v}) \) being the emission intensity at \( \tilde{v} \) (corrected to the number of photons emitted per unit wavenumber). The emission intensity can be obtained either from experiment or by computational simulation. The total radiative decay rate constant for the T1 \( \rightarrow S_{0} \) transition may then be written as:

\[
k_{sr}(T_{1} \rightarrow S_{0}) = \frac{8\pi^{2}\eta^{3}}{3\epsilon_{0}\hbar} |\mathbf{T}^{\text{eff}}(Q_{0}^{\text{T}})|^{2}
\]

The transition dipole moment \( \mathbf{T}^{\text{eff}}(Q_{0}^{\text{T}}) \) could be obtained by first-order perturbation interactions between the T1 \( \alpha \)-spin sub-state and the singlet excited state via spin–orbit coupling (SOC):

\[
\mathbf{T}^{\text{eff}}(Q_{0}^{\text{T}}) = \sum_{m,j=1,2} |\langle S_{m}^{\text{oc}}| \mathbf{S}_{j} \rangle|^{2} E(S_{m}) - E(T_{1}) \mathbf{M}_{s_{j}} / Q_{0}^{\text{T}}
\]

where the summation runs over all the normal modes, \( m \) are the Huang–Rhys factor and the effective high frequency mode \( \hbar \omega_{M} \) (corrected to the nearest integer), respectively:

\[
S_{m} = \sum_{j} S_{j}
\]

\[
n_{M} = \frac{\Delta E - \chi^{\text{FC}}}{\hbar \omega_{M}}
\]

Under the harmonic oscillator approximation, the intramolecular reorganization energy, \( \chi^{\text{FC}} \), could be estimated as:

\[
\chi^{\text{FC}} = \sum_{j} S_{j} \omega_{j}
\]

where the summation runs over all the normal modes, \( \omega_{j} \).

Non-radiative decay rate constant \( (k_{nr}) \)

In the limit of the Franck–Condon approximation in the non-adiabatic regime, the non-radiative decay rate constant \( (k_{nr}) \) of the T1 \( \rightarrow S_{0} \) transition can be estimated by application of the Fermi’s Golden Rule expression, assuming that both electronic states are harmonic:

\[
k_{nr}(T_{1} \rightarrow S_{0}) = \frac{2\pi}{\hbar} \langle T_{1}|H_{\text{SOC}}|S_{0}\rangle^{2} \sum_{m} S_{m}^{\text{nr}} \frac{1}{n_{M}^{\text{nr}}} \exp(-S_{M}) \exp\left(\frac{(\Delta E - n_{M} \hbar \omega_{M} - \chi^{\text{FC}})^{2}}{4\chi^{\text{FC}} \hbar B_{T}}\right)
\]

This expression can be applied when \( \hbar \omega_{M} \gg k_{B}T \) and the solvent orientational and librational motions are treated classically. \( \omega_{ab} \) are the high-frequency (hf) intraligand vibrational modes (\( \hbar \omega_{ab} \gg 1000 \text{ cm}^{-1} \)), typically corresponding to the aromatic CC/CN stretching modes (\( \hbar \omega_{ab} \sim 1200-1500 \text{ cm}^{-1} \)) and C===C stretching modes (\( \hbar \omega_{C==C} \sim 2200-2300 \text{ cm}^{-1} \)) if the acetylide ligand is involved in the complex; \( \gamma_{S} \) is the solvent reorganization energy and may be obtained from eqn (2); \( \Delta E \) is given by

\[
\Delta E = \Delta E_{00} - \chi^{\text{FC}}
\]

with \( \Delta E_{00} \) being the zero-point energy difference between the T1 and \( S_{0} \) states and \( \lambda_{i} \) being the reorganization energy contributed by the low-frequency (lf) modes of the complex (i.e., \( \hbar \omega_{ab} < 1000 \text{ cm}^{-1} \)). Assuming that all the normal modes are harmonic oscillators,

\[
\lambda_{i} = \sum_{j} S_{j} \hbar \omega_{j}
\]

where the summation runs over all the normal modes, \( \omega_{j} \).

Computational details

In this work, the hybrid density functional, PBE0, \( ^{15} \) was employed for all calculations using the program package G09. \( ^{16} \) The 6-31G* basis set \( ^{17} \) was used for all atoms except Au, which was described by the Stuttgart relativistic pseudopotential and its accompanying basis set (ECP60MWB). \( ^{18} \) The solvent effect was also included by means of the polarizable continuum model (PCM) with the solvent as dichloromethane (CH2Cl2; \( \eta = 1.424 \)). \( ^{19} \) Geometry optimizations of the singlet ground state (S0) and the lowest triplet excited state (T1) were respectively carried out using restricted and unrestricted density functional theory (i.e., RDFT and UDFT) formalisms without symmetry constraints. Frequency calculations were performed on the optimized structures to ensure that they were minimum energy structures by the absence of imaginary frequency (i.e., Nvib > 0). Stability calculations were also performed for all the optimized structures to ensure that all the wavefunctions obtained were stable.

Vertical transition energies were computed using the linear response approximation for absorption, but the state specific approach for emission. \( ^{20} \) For the radiative decay rate constant calculation (using eqn (8) and (9)), the singlet excited state energy, \( E(S_{m}) \), the associated transition dipole moment of the
Results and discussion

Ground state structures and absorption energies

In general, the optimized ground state structures of 1, 3-exo, and 3-endo are in good agreement with the X-ray crystallography data (<0.05 Å and 8.5°) except for the dihedral angle between the planes of the [C=N=C] ligand and the phenyl ring of the acetylide ligand (δ); calculations revealed a nearly coplanar geometry (δ ~ 5.7° and 0.27° for 1 and 3-exo respectively) whereas experimentally determined δ values are 66.1° and 54° respectively.3e,lb Similarly, though DFT calculations predict a non-coplanar geometry for the ground state of 3-endo (δ ~ 130°), the corresponding X-ray data is only ~59° (see ESI† for the X-ray data and DFT results for 3-endo). In addition, the Au–C(acetylide) distance for 1 was calculated to be 1.950 Å while the corresponding distance from the crystallography data is 2.009 Å.2a It should be noted that the Au–C(acetylide) distances reported for similar [(Cn=N)AuC≡CPh-4-Y] (Y is a substituent) complexes are in the range of 1.945–1.980 Å,2b our calculated value falls within this range. It is thus possible that the discrepancies between experimental and calculated geometries are due to the crystal packing effect.

Table 2 presents the absorption energies of low-lying singlet excited states at the respective optimized S0 geometries of the four complexes studied herein. A full list of the TD-DFT results can be found in the ESI. In general, the calculated absorption energies are in good agreement with the corresponding experimental absorption peak maxima. Previous TD-B3LYP/PCM calculations also suggest that the lowest absorption peak of 1 is 1LLCT in nature (LLCT = ligand-to-ligand charge transfer), with a calculated vertical excitation energy at λ = 408 nm (f = 0.23).2a

As depicted in Table 2, the most conspicuous difference among the four complexes is that, except for 3-exo, the first singlet excited state (S1) is a 1LLCT excited state, derived mainly from the HOMO → LUMO transition, [1π*(C=N=C) − π*(C=N=C)] (Fig. 2 and ESI† for the MO surfaces). On the other hand, for 3-exo, the S1 state is predominantly intraligand (IL) in character (~80%); this 1IL excited state is derived from the H → 1 → LUMO transition and is a 1ππ*(C=N=C) excited state. The difference in the nature of the S1 excited state among the four complexes can be rationalized as follows: upon increasing the π-conjugation along the series 1, 2, 3-endo, and 3-exo, H → 1 is destabilized and the MO splitting (Δε) between HOMO and H → 1 decreases from 0.62 eV (1) to 0.26 eV (3-endo) and 0.20 eV (3-exo), (Fig. 2). This decrease in MO splitting results in a decrease in the contribution of the HOMO → LUMO transition to the S1 state, but a concomitant increase in percentage of H → 1 → LUMO transition (Table S9).† As a result, the predominant contribution to the S1 state is mainly 1LLCT in character for 1, 2, and 3-endo, while for 3-exo, the S1 state is mainly 1IL in nature. This decrease in MO splitting not only affects the nature of the lowest singlet excited state, but also significantly impacts the emitting excited state, as described in a later section.

T1 excited state: radiative and non-radiative decay rates

The experimental photophysical data regarding the emissions of the four gold(I) complexes are listed in Table 3.

### Table 2

Singlet excited state energies (λ in nm) and the associated oscillator strengths (f), together with the nature of singlet excited states of the four complexes depicted in Chart 1 at their respective optimized S0 geometries. μGS(D) is the ground state dipole moment obtained from DFT calculations. The experimental values (λexp in nm) are listed in the last column.

<table>
<thead>
<tr>
<th>Complexes</th>
<th>Sm</th>
<th>λ</th>
<th>F</th>
<th>Naturea</th>
<th>μGS(D)</th>
<th>λexp</th>
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</thead>
<tbody>
<tr>
<td>1</td>
<td>S1</td>
<td>392</td>
<td>0.251</td>
<td>1LLCT</td>
<td>6.13</td>
<td>400, 380, 362</td>
</tr>
<tr>
<td>2</td>
<td>S1</td>
<td>367</td>
<td>0.0519</td>
<td>1ππ*(C=N=C)</td>
<td>8.36</td>
<td>396, 380</td>
</tr>
<tr>
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<td>S1</td>
<td>401</td>
<td>0.2737</td>
<td>1LLCT</td>
<td>8.09</td>
<td>428, 409</td>
</tr>
<tr>
<td>3-endo</td>
<td>S1</td>
<td>401</td>
<td>0.0787</td>
<td>1LLCT</td>
<td>8.25</td>
<td>409</td>
</tr>
</tbody>
</table>

a All the singlet excited states have some metal character, but generally less than 10%.
As depicted in Table 3, 1 has the fastest radiative and non-radiative decay rate constants, with the latter being more than 800-fold faster than that of the other three complexes. Complex 3-exo displays the slowest $k_{nr}$ among the four complexes studied herein, while the associated $k_{r}$ is comparable to the other two complexes with π-conjugation at the [C=N=C] cyclometalated ligand (i.e., 2 and 3-endo).

To understand the emission properties of the four complexes depicted in Chart 1, we have employed unrestricted DFT (UDFT) to optimize their lowest triplet excited states. For 2 and 3-exo, only one triplet excited state, $^3\pi\pi^*$ (C=N=C) IL excited state, was found. On the other hand, two triplet excited state minima, one $^3\text{IL}$ in character and the other $^3\text{LLCT}$ \((\pi[C(=CPh-4-OMe)] \rightarrow \pi^*[C=N=C])\), were found for both 1 and 3-endo. The electron difference density maps (eddms) for the calculated triplet excited states, together with the relative energy splitting between the $^3\text{IL}$ and $^3\text{LLCT}$ excited states for complexes 1 and 3-endo, are presented in Fig. 3.

Table 4 lists the computed 0-0 transition energies ($\Delta E_{00}$), vertical emission energies ($\Delta E_{\text{em}}^{\text{SS}}$, Fig. 1), Franck–Condon factor-weighted emission energies ($\langle \rho \rangle_{\text{FCF}}$), and radiative decay rate constants of the optimized $T_1$ excited states of the four gold(m) complexes studied herein.

(i) Emission energies. With the exception of 2, there is generally a close correlation between the experimental solution emission maxima ($\lambda_{\text{max}}$) at room temperature and the calculated $\Delta E_{00}$ of the $^3\text{IL}$ excited states of the gold(m) complexes in Chart 1. This suggests that for complexes 1, 3-exo, and 3-endo, the emission maximum may correspond to the 0-0 transition of $^3\text{IL} \rightarrow S_0$. The experimental emission maximum of 2 is at a lower energy than that of 3-exo (Table 3). For related platinum(m) [C=N=C] cyclometalated complexes, the one with a naphthalene moiety at the [C=N=C] ligand displays a higher energy emission peak than the one with a fluorene unit (e.g., complexes 7 and 8 in ref. 9) and the emitting triplet excited state is assigned as having a mixed $^3\text{IL}/^3\text{MLCT}$ character (MLCT = metal-to-ligand charge transfer). Our present theoretical analysis is in accordance with these findings on the platinum(m) [C=N=C] cyclometalated complexes: $\Delta E_{00}$ of the gold(m) complexes is in the order 1 > 2 > 3-endo > 3-exo. This trend is a manifestation of the increase in π-conjugation at the [C=N=C] cyclometalated ligand when one goes from 1 to 2 to 3-endo and 3-exo. Increasing π-conjugation destabilizes the $\pi(C=N=C)$ orbital, (see also Fig. 2), thereby decreasing the MO splitting between $\pi(C=N=C)$ and $\pi^*(C=N=C)$ orbitals and leading to a red shift in emission energy of the $^3\text{IL}$ excited state from 1 to 2 to 3-endo and 3-exo. The fact that the experimental emission maximum of 2 is lower in energy than those of 3-exo and 3-endo may reflect that the emission peak maximum of 2 may not correspond to the 0-0 transition; it may suggest that the structural distortion between the $T_1$ and $S_0$ states of 2 is larger than that of 3-exo and 3-endo (vide infra).
constant, which is not supported by the photophysical data. The geometries for the four complexes in Chart 1 (isovalue 0.001 a.u.) were optimized at the UDFT level, and the S0 ground-state geometries were obtained using SS-TDDFT calculations at their respective optimized T1 excited state geometries. The S0 ground-state geometries serve to quantify the structural distortion between the emitting triplet excited state and the ground state, the smallest values of S0 for 1, 3-exo, and 3-endo reveal that the uorene unit at the [C60] molecule imparts the greatest rigidity to the complex. In other words, the rigidity of the organic moiety at the pincer-type cyclometalated ligand is the greatest among the four gold(III) complexes.

(ii) Radiative decay rate constants. Table 4 presents the radiative decay rate constants calculated for each of the T1 excited states of the four complexes. Although the kᵣ values of the T1 excited states are slightly underestimated by a factor of 2.7–3.1, they are consistent with the experimental kᵣ values except in the case of 2 (compare Table 3 with 4). The calculations indicate that 2 should have the slowest radiative decay rate constant, which is not supported by the photophysical data recorded at room temperature (Table 3). However, it was reported that the emission lifetime of 2 increases from 25 µs at room temperature to 2285 µs in a glassy medium at 77 K. Assuming that this lifetime corresponds to the radiative lifetime, kᵣ would be estimated to have a maximum value of 438 s⁻¹. This is close to our theoretical results, i.e., the 3IL excited state of 2 should have the slowest radiative decay rate constant among the four gold(III) complexes. As a reference, the kᵣ estimated in the same way as that of 2 at 77 K would be 7.30 × 10⁴, 3.55 × 10⁴, and 2.46 × 10⁴ s⁻¹ for 1, 3-exo, and 3-endo respectively. It is conceivable that the emission of 2 at 298 K and 77 K originated from different excited states. However, no other triplet excited state minimum was found for compound 2 using the present DFT/TDDFT method.

(iii) Non-radiative decay rate constants. Table 5 lists the calculated results related to the non-radiative decay rate constants. First, let us consider the 3IL excited states of the four gold(III) complexes. As depicted in Table 5, the Huang–Rhys factors (Sₚ for 3IL) are in the order: 1 > 2 > 3-exo ∼ 3-endo. This trend is in line with the S₀ to T₁ structural distortion of the following organic molecules in the order: benzene > naphthalene > carbazole (carbazole is isoelectronic to fluorene). These two trends are similar because the 3IL excited states of these four gold(III) complexes are mainly localized on the phenyl, naphthalenyl, and fluorenyl moieties, respectively (Fig. 3). As the Huang–Rhys factor serves to quantify the structural distortion between the emitting triplet excited state and the ground state, the smallest values of Sₚ for 3-exo and 3-endo reveal that the fluorine unit at the [C₆₀] cyclometalated ligand imparts the greatest rigidity to the complex. In other words, the rigidity of the organic moiety at the pincer-type cyclometalated ligand could qualitatively account for the experimental results that 1 has the fastest non-radiative decay rate constant and 3-exo the slowest. Besides, the magnitude of the SOC matrix element between the 3IL excited state and S₀ ground state follows the order: 1 > 3-
3-endo > 3-exo > 2. At their respective optimized 3IL excited states, the metal contributions (expressed as $c_d^2$) to the H − 1 (HOMO for 3-exo and 3-endo), at their optimized T1 geometries, are 4.18 (1), 0.36 (2), 1.94 (3-exo), and 1.07 (3-endo), respectively. As SOC is mainly brought about by the gold(m) ion, the larger the coefficient of Au(d) in the H − 1/HOMO, the larger should be the SOC matrix element, $(4\hbar^2/|S_0|)^2$. The Au(d) character in the H − 1/HOMO of the gold(m) complexes studied herein is related to the nature of the HOMO of the C-deprotonated moiety in the [C=NC] ligand. For complex 2, the H − 1 is mainly localized on the long molecular axis of the naphthalene fragment (Fig. 2), thus rendering the [C$_{np}$=N=C] ligand to have little interaction with the gold(m) ion and therefore, the smallest $c_d$ in the H − 1 orbital of 2. On the other hand, the corresponding orbital of complex 3-exo is along the short molecular axis of the fluorene fragment, thus the [C$_d$=N=C] ligand could have a stronger interaction with the gold(m) ion, and hence, a larger $c_d$ in the HOMOs of complexes 3-exo and 3-endo.

Although both the effective Huang–Rhys factor $S_M$ and the SOC between the T1 and S0 states are largest for 1, the calculated non-radiative decay rate constant $k_{nr}$ for the $3\text{IL} \rightarrow S_0$ transition is smaller than that of 3-exo, a result contrary to the order of experimental $k_{nr}$ values; $k_{nr}$(calc): $2 > 3\text{-exo} > 1$; $k_{nr}$(exp): $1 \gg 2 > 3\text{-exo}$. This is because 1 has a much larger energy gap between the $3\text{IL}$ and S0 states than the other three gold(m) complexes (Table 4), making the energy gap effect play a dominant role in determining the $k_{nr}$ ($3\text{IL} \rightarrow S_0$) of 1. Similarly, the calculated non-radiative decay rate constant for 3-endo is ~1.25 × 10$^{-7}$ s$^{-1}$, which is also smaller than that of 3-exo, and is inconsistent with the experimental data (compare Tables 3 and 5). For these two complexes, 1 and 3-endo, an additional triplet excited state minimum was found (Fig. 3). This triplet excited state, as observed from the eddms in Fig. 3, is best characterized to be a $^3\text{LLCT}$, $\left[\pi(C\equiv\text{CPH}-4\text{-OMe}) \rightarrow \pi^\ast(C\equiv\text{NC})\right]$, excited state. This $^3\text{LLCT}$ excited state displays a large amplitude motion along the dihedral angle between the [C=NC] plane and the arylacetylide plane ($\delta$): from $\sim$−4.132° ($S_0$) to $\sim$88.739° $(^3\text{LLCT})$ for 1 and from 130.381° ($S_0$) to 92.352° $(^3\text{LLCT})$ for 3-endo (see Fig. 4 for the optimized structures of the $S_0$ and $^3\text{LLCT}$ excited states for complexes 1 and 3-endo).

Because of this large amplitude motion, we refrained from performing a Franck-Condon calculation on the $^3\text{LLCT} \rightarrow S_0$ transition, as we have performed for that of the $3\text{IL} \rightarrow S_0$. This is because, for the Franck–Condon calculation implemented in G09, the normal modes are represented in Cartesian coordinates. Cartesian coordinates are inadequate to describe large amplitude motions, such as torsions, as this could lead to artificial bond breaking and bond forming at its extreme. For instance, due to the rotation of the phenyl group at the arylacetylide ligand relative to the [C=NC] plane, the C-H bonds on the phenyl ring of the arylacetylide ligand would be artificially broken if Cartesian coordinates were used to describe the normal modes. This could result in erroneously large Huang–Rhys factors for the C–H stretching modes. However, in reality, there is no C–H bond breaking when one goes from the $^3\text{LLCT}$ to the $S_0$ state. Moreover, such fictitious bond breaking and bond forming will lead to a diffuse Duschinsky matrix, which could lead to an incorrect interpretation of the fast non-radiative decay rate constant due to a large Duschinsky effect.

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Table 5 Effective Huang–Rhys factors ($S_M$) for the high-frequency mode, intramolecular ($\lambda_m$) and solvent ($\lambda_s$) reorganization energies (in cm$^{-1}$), dipole moments of the T1 excited state ($\mu_{T1}$), $(T_1|H_{SOC}|S_0)^2$ (in cm$^{-1}$), Franck–Condon Factors (FCF), and non-radiative decay rate constants ($k_{nr} \times 10^5$ s$^{-1}$) for the four complexes studied herein.

| M         | 3IL     | 3-endo  | 3-exo  | 1       | $\lambda_m$ | $\lambda_s$ | $\mu_{T1}$ | $(T_1|H_{SOC}|S_0)^2$ | FCF  | $k_{nr}$ |
|-----------|---------|---------|--------|---------|-------------|-------------|------------|----------------------|------|----------|
| SS        | 2.889   | 2.388   | 2.622  | 2.27    | 21.2        | 9.32        | 0.22       | 2051 n.a.            | 1812 | 18.5     |
| FC        | 2.920   | 2.439   | 2.408  | 1.93    | 12.74       | 7.21        | 0.22       | 2051 n.a.            | 1812 | 18.5     |

$^a$ $S_M$ corresponds to the effective Huang–Rhys factor of the high-frequency (hf) modes in the range 1000 ≤ $\omega_{hf}$ ≤ 1800 cm$^{-1}$ when the T1 excited state is $^3\text{IL}$. $^b$ The intramolecular reorganization energy $\lambda_m$ was obtained in two different ways: state specific (SS; eqn (3)) and Franck–Condon (FC; eqn (13)). $^c$ $S_M = S_C$, i.e., the Huang–Rhys factor of the C=C stretching mode, $\omega_{C=C}$ (see ESI† for details). $^d$ Estimated under the assumption that the Huang–Rhys factors of the $^3\text{LLCT} \rightarrow S_0$ transition are the same as those of the $^3\text{IL} \rightarrow S_0$ of the same complex, together with the Huang–Rhys factor of the C=C stretching normal mode. $^e$ The term $2\pi/\hbar$ is absorbed into the FCF.

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Fig. 4 Optimized structures of the $S_0$ (left) and $^3\text{LLCT}$ excited states for 1 (top) and 3-endo (bottom).
Nevertheless, the C≡C stretching normal mode is decoupled from the other normal modes, as reflected by the Duschinsky matrix elements of the $^3\text{LLCT} \rightarrow S_0$ transition; $\alpha_{\text{C=C}}$ is the only normal mode that has the diagonal matrix element equal to 1. Therefore, we estimated the non-radiative decay rate constants of the $^3\text{LLCT}$ excited state by replacing all the Huang–Rhye factors ($S_j$) of the $^3\text{LLCT} \rightarrow S_0$ transition with those of the $^3\text{IL} \rightarrow S_0$ transition, but keeping the Huang–Rhye factor of the C≡C stretching normal mode from a Franck–Condon calculation of the $^1\text{LLCT} \rightarrow S_0$ transition. Such an assumption is based on the fact that both the $^3\text{LLCT}$ and $^3\text{IL}$ excited states of the gold(III) complexes involve changes in electron density at the [C$^\text{N}$C]–torsional motion between the [C$^\text{N}$C] and arylacetylide ligands.

These non-radiative decay rate constants may still be underestimated. The $^3\text{LLCT}$ energy gap is even wider. In fact, we have not been able to locate a T1 minimum corresponding to a barrier width, leading to a significant increase in the FCFs, and, hence, a further enhancement of the non-radiative decay rate.

If one supposes that the torsional motion increases the FCF of the $^3\text{LLCT} \rightarrow S_0$ transition by a factor of $\sim 10^2$ and $\sim 10^7$ s$^{-1}$, respectively. We may then re-estimate the non-radiative decay rate constants by taking into consideration both the $^3\text{LLCT}$ and $^3\text{IL}$ excited states with Boltzmann populations. As $^3\text{LLCT}$ is calculated to be $\sim 500$ cm$^{-1}$ below $^3\text{IL}$ for complex 1, the re-estimated non-radiative decay rate constant for complex 1 at room temperature is comparable to the experimental value ($k_{\text{nr}}(\text{calc}) \sim 1.6 \times 10^7$ s$^{-1}$ and $k_{\text{nr}}(\text{exp}) \sim 5.9 \times 10^7$ s$^{-1}$). In other words, the major deactivating channel for the emissive excited state of 1 is not $^1\text{dd}$ or $^1\text{LMCT}$, as is usually ascribed to efficient non-radiative decay for luminescent transition metal complexes, but $^3\text{LLCT}$ due to a large SOC, a large solvent reorganization energy, and the non-planar torsional motion between the [C$^\text{N}$C] and arylacetylide ligands. For $^3\text{endo}$, the $^3\text{LLCT}$ excited state is calculated to be $\sim 1400$ cm$^{-1}$ above that of the $^3\text{IL}$ state. Therefore, the re-estimated $k_{\text{nr}}$ becomes $\sim 1.5 \times 10^4$ s$^{-1}$, which is in good agreement with the values derived from the experimental measurements in solutions at $298$ K ($k_{\text{nr}}(\text{exp}) \sim 6.8 \times 10^3$ s$^{-1}$).

Based on the above analyses on non-radiative decay rate constants, it is the presence of the close-lying $^3\text{LLCT}$ excited state that contributes to the very fast non-radiative decay rate. The relative order of the $^3\text{LLCT}$ and $^3\text{IL}$ excited states would thus be important in determining the phosphorescence efficiency. In the present series of gold(III) complexes, this relative order can be understood from the relative energies of the $^3\text{IL}$ and $\pi(\text{C=CPh-4-OMe})$ MOs. As the $^3\text{LLCT}$ excited state is a charge transfer excited state, while the $^3\text{IL}$ excited state is localized, the singlet-triplet splitting of LLCT excited states ($E(^3\text{LLCT}) - E(^3\text{IL})$) would be smaller than that of IL excited states ($E(^3\text{IL}) - E(^1\text{IL})$). In the case of 1, due to the large orbital energy difference ($\Delta E$) between the $\pi(\text{C=CPh-4-OMe})$ and $\pi(\text{C=CPh-4-OMe})$ MOs (Fig. 2), the $^1\text{IL}$ excited state is much higher in energy than that of the $^3\text{LLCT}$ excited state. Thus, the splitting of the $^3\text{IL}$ and $^3\text{LLCT}$ states is the smallest (see Fig. 6 for a schematic illustration). For $^3\text{endo}$, as the corresponding $\Delta E$ is smaller than that of 1, the $^3\text{LLCT}$ is only slightly lower in energy than the $^3\text{IL}$ excited state such that the $^3\text{IL}-^3\text{LLCT}$ energy gap widens. For $^3\text{exo}$, as the lowest singlet excited state is predominantly IL in character, the $^3\text{IL}$-$^3\text{LLCT}$ energy gap is even wider. In fact, we have not been able to locate a $T_1$ minimum corresponding to a $^3\text{LLCT}$ excited state (Fig. 6).

Based on the above rationale, it is speculated that the $^3\text{IL}$-$^3\text{LLCT}$ gap of 2 should fall between that of 1 and $^3\text{endo}$, as...
deduced from the relative order of the $\pi(C_{\text{np}}^N\text{N} \text{C})$ and $\pi(C \equiv \text{CPh-4-OMe})$ MOs depicted in Fig. 2. Indeed, an energy minimum of a $^3\text{LLCT}$ excited state was located in the course of LR-TDDFT optimization; subsequent SS-TDDFT calculation at this geometry showed that this $^3\text{LLCT}$ excited state is lower-lying than the $^3\text{IL}$ one. However, global hybrid density functionals, (e.g., PBE0, a functional that we have employed in the present work) generally underestimate the energy of charge transfer excited states within the TDDFT framework. Thus, we performed UDFT optimization starting from these TDDFT-optimized structures (which have a stable wavefunction) to see if there is a $^3\text{LLCT}$ excited state minimum. Unfortunately, UDFT optimization starting from the TDDFT-optimized $^3\text{LLCT}$ excited state went back to the $^3\text{IL}$ excited state. It is likely that this $^3\text{LLCT}$ excited state is metastable and exhibits vibronic coupling with other close-lying excited states.

Conclusions

We have carried out a detailed theoretical study on four gold(III) [C$^N\text{N} \text{C}$] cyclometalated complexes with different extents of $\pi$-conjugation. It is commonly prescribed that a rigid ligand in a transition metal complex can minimize structural distortion between the emitting triplet excited state and the ground state, thereby decreasing the non-radiative decay rate. Franck–Condon analyses on the $^3\pi-^3\pi^\ast$($C^N\text{N} \text{C}$) IL $\rightarrow S_0$ transitions of the four gold(III) complexes confirmed that an increase in $\pi$-conjugation at the [C$^N\text{N} \text{C}$] cyclometalated ligand results in a more rigid transition metal complex, as reflected by the effective Huang–Rhys factor, $S_{\text{eff}}$: $1 > 2 > 3$-exo and 3-endo. Although this trend correlates with the experimentally determined non-radiative rate constants, $1 \gg 2 > 3$-exo, the calculated $k_{\text{nr}}$ of the $^3\text{IL}$ $\rightarrow S_0$ transition is inconsistent with the experimental data if one also takes into consideration the $^3\text{IL}-S_0$ energy gap. DFT/TDDFT calculations reveal that there is an additional triplet excited state minimum, $^3\pi(C \equiv \text{CPh-4-OMe}) \rightarrow ^3\pi^\ast(C^N\text{N} \text{C})$] LLCT, for complexes 1 and 3-endo, but not for 3-exo. It was
found that the non-radiative decay rate constant for this $^3LLCT \rightarrow S_0$ transition exceeds $10^7 \text{ s}^{-1}$, which is more than three orders of magnitude faster than the $k_{nr}$ for the $^1L\rightarrow S_0$ transition. More importantly, if the relative splitting between the $^3LLCT$ and $^1L$ excited states was included in estimating the $k_{nr}$ of complexes 1 and 3-endo, the calculated and experimental $k_{nr}$ are in quantitative agreement. Based on the analysis of the relative order of $\pi(C^\equiv N^\equiv C)$ and $\pi(C^\equiv CPh-4-OMe)$ MOs, one could rationalize why complexes 1 and 3-end, but not 3-exo, have low-lying $^3LLCT$ excited states. Our present analysis highlights the importance of the relative order of the frontier MOs of the coordinating ligands in multi-chromophoric transition metal complexes in designing strongly luminescent transition metal complexes. It also challenges the presumption that the low phosphorescence efficiency of transition metal complexes is due to the close proximity of the dd ligand-field state to the emitting triplet excited state.

Appendix

List of definitions, abbreviations, and symbols

<table>
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<tr>
<th>Abbreviation</th>
<th>Definition</th>
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<tbody>
<tr>
<td>IL</td>
<td>Intraligand</td>
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<tr>
<td>LLCT</td>
<td>Ligand-to-ligand charge transfer</td>
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<tr>
<td>LMCT</td>
<td>Ligand-to-metal charge transfer</td>
</tr>
<tr>
<td>MLCT</td>
<td>Metal-to-ligand charge transfer</td>
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<td>SOC</td>
<td>Spin-orbit coupling</td>
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<td>Equilibrium</td>
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<td>Non-equilibrium</td>
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<td>PCM</td>
<td>Polarizable continuum model</td>
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<td>FCF</td>
<td>Franck-Condon factor</td>
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<td>PES</td>
<td>Potential energy surface</td>
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<td>eddm</td>
<td>Electron difference density map</td>
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<tr>
<td>$\mu$G</td>
<td>Dipole moment of the ground state</td>
</tr>
<tr>
<td>$\mu^T$</td>
<td>Dipole moment of the T1 excited state</td>
</tr>
<tr>
<td>$c_d$</td>
<td>Coefficient of Au(d-orbital)</td>
</tr>
<tr>
<td>$Q_G$</td>
<td>Optimized ground state (GS) geometry</td>
</tr>
<tr>
<td>$Q^{ES}_{GS}$</td>
<td>Optimized excited state (ES) geometry</td>
</tr>
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<td>$\Delta E_{em}^{SS}$</td>
<td>Energy emission evaluated within the state-specific (SS) approach; eqn (1), Fig. 1</td>
</tr>
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<td>$E_{EQ}^{ES}(Q^{ES}_{GS})$</td>
<td>Energy of the excited state (ES) with equilibrium (EQ) solvation at the optimized excited state geometry, Fig. 1</td>
</tr>
<tr>
<td>$E_{NEQ}^{ES}(Q^{ES}_{GS})$</td>
<td>Energy of the ground state (GS) with non-equilibrium (NEQ) solvation at the optimized excited state geometry, Fig. 1</td>
</tr>
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<td>Solvent reorganization energy; eqn (2)</td>
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<td>Intramolecular reorganization energy evaluated within the state-specific (SS) approach; eqn (3)</td>
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<tr>
<td>$\lambda^{MC}$</td>
<td>Intramolecular reorganization energy obtained from Franck-Condon (FC) calculation; eqn (13)</td>
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Notes and references

