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Dissertation

Theoretical Study on the Excited States and Emission Mechanisms of Metal Complexes with Multiple-Emissions

(多重発光を示す金属錯体の励起状態と発光機構に関する
理論的研究)

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Chapter 1: General Introduction

1.1. Metal Complexes

Metal complexes consist of metal atoms and non-metal compounds (called as ligand; mostly organic compounds) where d orbitals of the metal atom are split by the repulsion from the ligand. The splitting pattern of d orbitals normally characterizes geometrical structures of the metal complex (Figure 1). To resolve the splitting pattern of d orbitals, an electrostatic crystal field theory and a ligand field theory have been established. The electrostatic crystal field theory is based on an assumption that a bond between a metal atom and ligand has an ionic character, but it is known that some complexes have a covalent bond. Considering the exception, the ligand field theory is employed to analyze an interaction between d orbitals of a metal atom and orbitals of a ligand (e.g., σ , π) like in a molecular orbital theory. For CO ligand, as an example, d orbitals are stabilized because the electron density of a metal atom decreases by π back donation to π^* orbital of CO. These theories can make us understand a spectrochemical series which shows the magnitude of the splitting of d orbitals by a ligand.

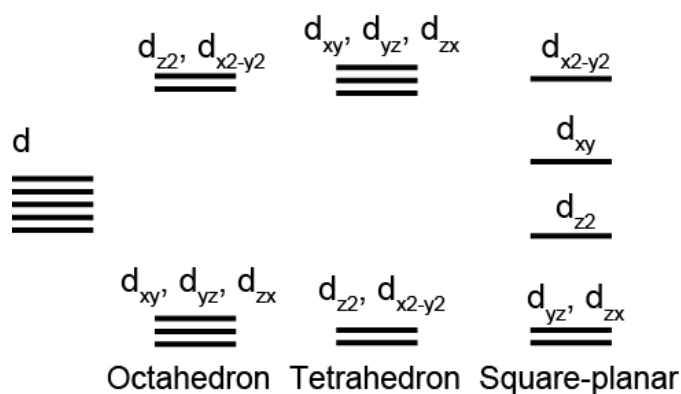


Figure 1. Schematic splitting patterns of d orbitals in metal complexes.

Metal complexes have unique excited states related to an electron transfer between a metal atom and ligands (e.g. metal-to-ligand charge transfer, ligand-to-metal charge transfer) and a metal-metal interaction (e.g. mixed metal-to-ligand charge transfer, Figure 2).¹⁻³ Photophysical properties of the metal complexes such as photocatalyst,⁴⁻⁶ photoisomerization⁷ which appear in the excited states are different from those of the organic and inorganic

compounds except some cases because photochemical reactions generally go through the excited states.

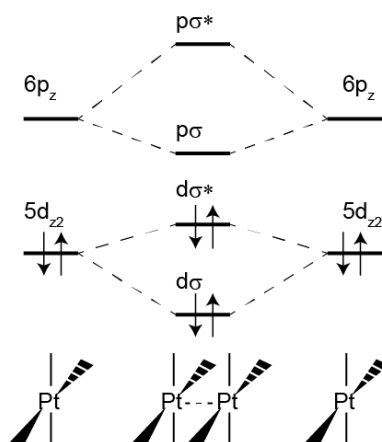


Figure 2. Simplified MO diagram showing mixed metal-to-ligand charge transfer in dimer of a square platinum complex.

In particular, photoluminescence of the metal complexes has been also paid attention as one of hot topics in photochemistry for several decades. Organic and inorganic molecules have been known to show fluorescence, whereas the metal complexes show both fluorescence and phosphorescence^{8,9} because the heavy metal atom facilitates the intersystem crossing from singlet to triplet states. The photoluminescence of the metal complexes is enhanced by the metal atom and it can be tuned easily by the metal atom or the ligand in comparison with organic compounds. In addition, the photoluminescence of metal complexes is sensitive to the external environment, which is known as a chromism (e.g. vapochromism,^{10,11} mechanochromism,^{12–14} solvatochromism,¹⁵ thermochromism,^{16,17} photochromism^{18,19}). Cu(I) complexes are known to show thermally activated delayed fluorescence that is caused in the lowest singlet state through triplet states.²⁰ Metal complexes such as Ir(III), Pt(II) and Ru(II) complexes are used as oxygen sensors^{21–23} and/or organic light emitting diodes^{24,25} unlike organic and inorganic molecules because the phosphorescence is quenched by an oxygen²⁶ and induces organic light emitting efficiency that electroluminescent device will form 25% singlet and 75% triplet excitons.²⁷ Lanthanide complexes have also been studied widely due to an advantage having a sharp emission with a longer lifetime ($\sim$ millisecond order) than other metal complexes.^{28,29}

1.2. Multiple-Emissions

The photoluminescence generally occurs in the lowest excited singlet or triplet states according to Kasha's rule that the rate of relaxation and internal conversion is faster than that of emission in the excited states. In contrast, some molecules such as an azulene derivative³⁰ and a naphthalene derivative³¹ show multiple-emissions which is ascribed to the higher excited states preventing the Kasha's rule, because the rate of internal conversion to the lower excited state becomes slower due to a large energy gap (Figure 3). The multiple-emission can also occur due to several minima in the lowest excited states due to various intra- and inter-molecular interactions (e.g. π - π stacking, hydrogen bonding) which obey the Kasha's rule; as example, a pyrene derivative³² shows a dual emission which are caused by monomer and excimer (Figure 4). As discussed above, the mechanism of multiple-emissions is categorized into two types. Considering these two types, I investigate the lowest and higher excited states involving emission which violates the Kasha's rule, and also several minima in the lowest excited states under the Kasha's rule.

Comparing with the molecule showing single-emission, the molecules showing multiple-emissions should have more potential as materials for bioimaging,³³ sensors³² and organic electronics;³⁴ we can do a ratiometric measurement and generate a white light. However, it is not an easy task to design metal complexes showing multiple-emissions because there are scarce reports about the metal complexes with the multiple-emissions ascribed to the triggers such as the above cases. Also, the excited states of metal complexes should have a very complex character due to charge transfer between metal atoms and ligands. Therefore, developing the new metal complexes with the multiple-emissions has a great significance, and also theoretical approach is required to reveal the mechanism of multiple-emissions, as well as the related excited states and the role of metal atoms for molecular design.

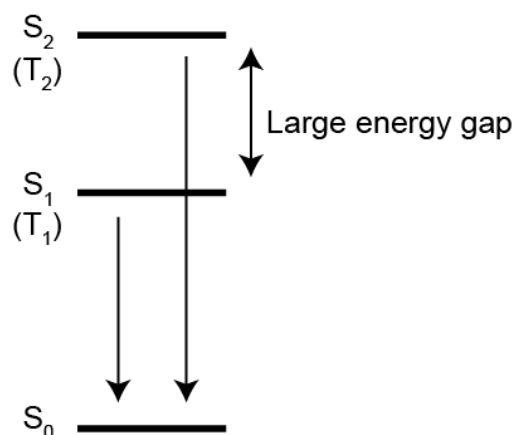


Figure 3. Schematic energy diagram showing multiple-emissions caused by S_1 (T_1) and S_2 (T_2) states which prevents the Kasha's rules.

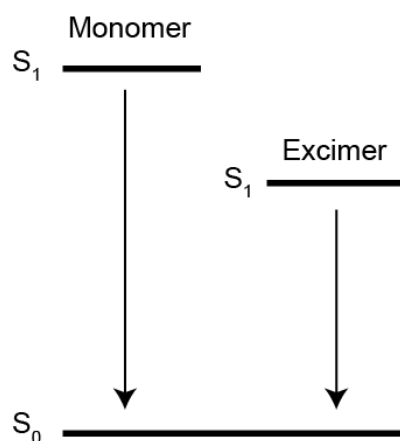


Figure 4. Schematic energy diagram showing multiple-emissions caused by monomer and excimer of a pyrene derivative in the S_1 state obeying the Kasha's rules.

1.3. DFT and TDDFT Calculations

As the rapid progress in computer hardware and molecular theory, it becomes feasible to carry out theoretical calculations for many phenomena of metal complexes. As molecular theory, density functional theory (DFT) for electronic parts in molecules is one of the most successful approach. In 1927, Thomas and Fermi approached to a quantum statistical model of electrons, taking into account only a kinetic energy even if nuclear-electron and electron-electron contributions exist in a completely classical way (Thomas-Fermi model). They defined a kinetic energy term

by the following equation.

$$T_{TF}[\rho(\mathbf{r})] = C \int \rho^{\frac{5}{3}}(\mathbf{r}) d\mathbf{r} \quad (C \text{ is a constant})$$

The Tomas-Fermi expression for the energy of an atom is described by combining with the classical expression for the nuclear-electron Coulomb attraction potential and the electron-electron repulsion potential.

$$E_{TF}[\rho(\mathbf{r})] = C \int \rho^{\frac{5}{3}}(\mathbf{r}) d\mathbf{r} - Z \int \frac{\rho(\mathbf{r})}{r} d\mathbf{r} + \frac{1}{2} \iint \frac{\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)}{r_{12}} d\mathbf{r}_1 d\mathbf{r}_2 \quad (Z \text{ is an atomic number})$$

In 1964, Hohenberg and Kohn proposed two theories as a basis of the DFT which proves the accuracy of the Tomas-Fermi expression. One is that the electron density and the external potential are one-to-one correspondence and the energy can be described by the functional for the electron density (the first Hohenberg-Kohn theorem). The other is that the electron energy related to the density is obtained by minimizing the variational expression (the second Hohenberg-Kohn theorem).

In 1965, Kohn and Sham derived an equation (referred to as Kohn-Sham equation) for one-electron orbital function (Kohn-Sham orbital) shown below,

$$\left[-\frac{1}{2} \nabla^2 + V(\mathbf{r}) + \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + V_{xc} \right] \varphi_i(\mathbf{r}) = \varepsilon_i \varphi_i(\mathbf{r}) \quad (V_{xc} = \frac{\delta E_{xc}(\rho(\mathbf{r}))}{\delta \rho(\mathbf{r})})$$

$$E_{xc} \equiv T[\rho] - T_s[\rho] + V_{ee}[\rho] - J[\rho] = V_{ee}[\rho] - J[\rho] \text{ in general assumption}$$

The Kohn-Sham equation has an analogy with the Hartree-Fock equation which is derived through an independent particle approximation to the electronic Schrodinger equation (the total electronic wavefunction is approximated by a single Slater determinant). E_{xc} is called an exchange-correlation energy functional which cannot be handled exactly and is represented by various approximations, i.e. LDA (Local Density Approximation), GGA (Generalized Gradient approximation), meta-GGA, hybrid-GGA, semi-empirical and progressive functionals. The one-electron Kohn-Sham orbital function is usually written by a linear combination of basis functions of finite size, called as a basis set,

$$\varphi_i(\mathbf{r}) = \sum_i C_i \phi_i \quad (C \text{ is an orbital coefficient and } \phi \text{ is a basis function})$$

As a basis function, the Slater-type orbital ($e^{-\zeta r}$) well reproduce the atomic orbital feature, but the computational cost for molecular integral becomes high. To overcome this situation, a contracted function of Gauss type orbital,

e^{-ar^2} , is used to maintain the accuracy and relatively low computational cost. The core electrons normally do not participate in chemical bonding, and thus, an effective core potential which treats core electrons as a potential is often used for heavy elements. To describe the chemical bonding well, polarization and diffuse functions are included in a basis set.

To calculate the electronically excited states, a time-dependent DFT has also been developed. In 1984, Runge and Gross proved that the Hohenberg-Kohn theorem is valid even if a system depends on time (Runge and Gross theorem).

$$\left[-\frac{1}{2}\nabla^2 + V(\mathbf{r}, t) + \int \frac{\rho(\mathbf{r}', t)}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + V_{xc} \right] \varphi_i(\mathbf{r}, t) = \varepsilon_i \varphi_i(\mathbf{r}, t) \quad (V_{xc} = \frac{\delta E_{xc}(\rho(\mathbf{r}))}{\delta \rho(\mathbf{r})})$$

To improve the computational accuracy with retention of computational costs, de-excitation type solutions are also used, and an operator equation is represented under the equation.

$$\begin{pmatrix} A & B \\ B & A \end{pmatrix} \begin{pmatrix} X \\ Y \end{pmatrix} = \omega \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \begin{pmatrix} X \\ Y \end{pmatrix}$$

$$A_{ia,ib} = \delta_{ij} \delta_{ab} (\varepsilon_a - \varepsilon_i) + (ai||jb)$$

$$B_{ia,jb} = (ai||bj)$$

where ω denotes an eigenvalue which corresponds to an excitation energy. Though long years, DFT and TDDFT calculations have been employed for actual molecular system.

1.4. Photochemical Reactions

By irradiating to molecules, photochemical reactions occur through the excited states. When photochemical reaction mechanism is elucidated, one can propose new phenomena related to the photochemical reactions. Jablonski diagram is an energy diagram which shows a scheme of photochemical process (Figure 5). At first, molecules absorb the photon energy and excited from ground states to excited states, according to the Fermi's golden rule:

$$w_{if} = \frac{2\pi |V_{fi}|^2}{\hbar} \rho(E_i) \quad (V_{fi} = \langle \Psi_i | h | \Psi_f \rangle)$$

The radiation rate constant from S_0 to S_n state (k_r) is represented by the following equation,

$$k_{r, S_0 \rightarrow S_n} = \frac{2\pi}{\hbar} |\langle \Psi_{S_0} | h | \Psi_{S_n} \rangle|^2 \sum_S |\langle \chi_{S_0} | \chi_{S_n} \rangle|^2 \delta(E_{S_0} - E_{S_n})$$

The term, $\langle \chi_{S_0} | \chi_{S_n} \rangle$, is a Franck-Condon factor which denotes the overlap of nuclear wave functions in the

electronically ground and excited states. Moreover, k_r is also related to an oscillator strength f as

$$k_r = \frac{2\pi e^2 \nu^2}{\epsilon_0 m c^3} f$$

where f can be obtained from the ratio between transition dipole moment (μ_{mn}) and oscillating electric dipole moment induced by an electron under the harmonic vibration (μ_0).

$$f = \frac{|\mu_{mn}|^2}{|\mu_0|^2} = \frac{8\pi^2 m \nu}{3 h e^2} |\mu_{mn}|^2$$

$$\mu_{mn} = -\langle \Psi_m(\mathbf{r}) | \sum_i e \mathbf{r}_i | \Psi_n(\mathbf{r}) \rangle$$

The maximum value of f equals to 1, and a very small f means a forbidden transition. The electronic transition between the states of the same symmetry (e.g. gerade to gerade) cannot occur because the μ_{mn} has a zero value according to the Laporte rule. Also, the spin selection rule indicates that the electronic transition is allowed in the same spin multiplicity.

After the excitation, a relaxation and an internal conversion (IC) processes to the lowest singlet excited state (S_1 state) occur with accompanying a nonadiabatic transition between the electronic states of the same spin multiplicity. Then, the molecules show an emission as a fluorescence with an oscillator strength which can be calculated by the above equation. The nonradiative transition from singlet to triplet state is called as an intersystem crossing (ISC) process. When the ISC process is accelerated, phosphorescence is caused in the T_1 state. The ISC process is governed by a spin-orbit-coupling (SOC). The rate of $S_i \rightarrow T_f$ ISC process can be derived under the Fermi's golden rule. The SOC operator (h^{SOC}) is represented as orbital angular momentum ($\mathbf{l}$) multiplied by spin angular momentum ($\mathbf{s}$).

$$k_{S_i \rightarrow T_f} = \frac{2\pi}{\hbar} |\langle \Psi_{S_i} | h^{SOC} | \Psi_{T_f} \rangle|^2 \sum_T \left| \langle \chi_{S_i} | \chi_{T_f} \rangle \right|^2 \delta(E_{S_i} - E_{T_f})$$

$$h^{SOC} = C \mathbf{l} \cdot \mathbf{s} \quad (C \text{ is a constant})$$

Some organic molecules are known to show the ISC process according to the El-Sayed rule, indicating that the rate of the ISC process between $n\pi^*$ and $\pi\pi^*$ transition states is relatively large. In contrast, many metal complexes show phosphorescence because of a heavy atom effect, which induces the ISC process. The oscillator strength of the phosphorescence can be calculated under the equation.

$$f_{T_i \rightarrow S_0} = \frac{2m_e}{3\hbar^2} (E_{T_1} - E_{S_0}) \left| \sum_{S_n} \frac{\langle \Psi_{T_1} | h^{SOC} | \Psi_{S_n} \rangle \langle \Psi_{S_n} | e\mathbf{r} | \Psi_{S_0} \rangle}{E_{T_1} - E_{S_n}} - \sum_{T_n} \frac{\langle \Psi_{T_1} | e\mathbf{r} | \Psi_{S_n} \rangle \langle \Psi_{T_n} | h^{SOC} | \Psi_{S_0} \rangle}{E_{T_n} - E_{S_0}} \right|^2$$

The relaxation, IC, and ISC processes among S_0 , S_1 and T_1 states have been discussed by using a concept of conical intersection (CI), thanks to the development of theoretical techniques; the transition from the higher to lower states occurs at a geometry where two electronic states get close to each other. Thus, theoretical approach can reveal fundamental aspects of the metal complexes, i.e., their excited states, relaxation process, IC and ISC processes, and photoluminescence quantum yield.^{35–41}

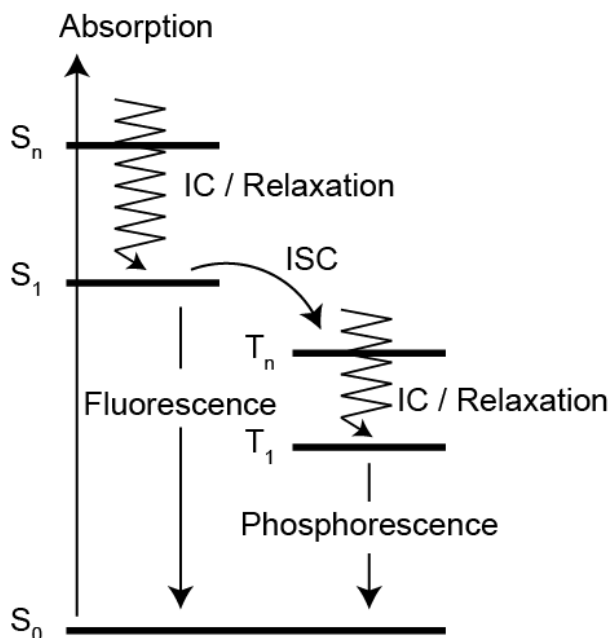


Figure 5. Jablonski diagram which shows an energy diagram for photochemical process.

1.5. This Work

In this thesis, I examine the excited states and emission mechanisms of the metal complexes with the multiple-emissions by DFT and TDDFT calculations to obtain insights into designing new functional materials. In Chapter 2, I investigate gold-thiolate clusters of $[\text{Au}_{25}(\text{SR})_{18}]^-$ ($\text{R} = \text{Me}$, EtPh: methyl, phenylethyl) with the multiple-emissions related to both the lowest and higher excited states. In Chapter 3, I focus on the excited state intramolecular proton transfer (ESIPT) and calculated for $[\text{Zn}(\text{hqxc})_2(\text{DMSO})_2]$ ($\text{hqxc} = 3\text{-hydroxy-2-quinoxalinecarboxylate}$, $\text{DMSO} =$

dimethylsulfoxide) complex which shows the multiple-emission involved in several minima in the lowest excited states via the ESIPT. Approaching to these two types of mechanisms of multiple-emission, I would like to support the synthesis of the metal complexes with the multiple-emissions for future new functional materials.

References

- (1) Vogler, A.; Kunkely, H. Excited State Properties of Transition Metal Phosphine Complexes. *Coord. Chem. Rev.* **2002**, 230 (1–2), 243–251.
- (2) Barbieri, A.; Accorsi, G.; Armaroli, N. Luminescent Complexes beyond the Platinum Group: The d¹⁰ Avenue. *Chem. Commun.* **2008**, 0 (19), 2185–2193.
- (3) Yoshida, M.; Kato, M. Regulation of Metal–metal Interactions and Chromic Phenomena of Multi-Decker Platinum Complexes Having π -Systems. *Coord. Chem. Rev.* **2018**, 355, 101–115.
- (4) Arias-Rotondo, D. M.; McCusker, J. K. The Photophysics of Photoredox Catalysis: A Roadmap for Catalyst Design. *Chem. Soc. Rev.* **2016**, 45 (21), 5803–5820.
- (5) Fukuzumi, S.; Lee, Y. M.; Nam, W. Thermal and Photocatalytic Production of Hydrogen with Earth-Abundant Metal Complexes. *Coord. Chem. Rev.* **2018**, 355, 54–73.
- (6) Kuramochi, Y.; Ishitani, O.; Ishida, H. Reaction Mechanisms of Catalytic Photochemical CO₂ Reduction Using Re(I) and Ru(II) Complexes. *Coord. Chem. Rev.* **2018**, 373, 333–356.
- (7) Wezenberg, S. J.; Chen, K. Y.; Feringa, B. L. Visible-Light-Driven Photoisomerization and Increased Rotation Speed of a Molecular Motor Acting as a Ligand in a Ruthenium(II) Complex. *Angew. Chemie - Int. Ed.* **2015**, 54 (39), 11457–11461.
- (8) Evans, R. C.; Douglas, P.; Winscom, C. J. Coordination Complexes Exhibiting Room-Temperature Phosphorescence: Evaluation of Their Suitability as Triplet Emitters in Organic Light Emitting Diodes. *Coord. Chem. Rev.* **2006**, 250 (15–16), 2093–2126.
- (9) Hofbeck, T.; Lam, Y. C.; Kalbáč, M.; Zálíš, S.; Vlček, A.; Yersin, H. Thermally Tunable Dual Emission of the d⁸-d⁸ Dimer [Pt₂(μ -P₂O₅(BF₂)₂)₄]₄⁻. *Inorg. Chem.* **2016**, 55 (5), 2441–2449.

- (10) Wenger, O. S. Vapochromism in Organometallic and Coordination Complexes: Chemical Sensors for Volatile Organic Compounds. *Chem. Rev.* **2013**, *113* (5), 3686–3733.
- (11) Kobayashi, A.; Kato, M. Vapochromic Platinum(II) Complexes: Crystal Engineering toward Intelligent Sensing Devices. *Eur. J. Inorg. Chem.* **2014**, *2014* (27), 4469–4483.
- (12) Kojima, M.; Taguchi, H.; Tsuchimoto, M.; Nakajima, K. Tetradentate Schiff Base-Oxovanadium(IV) Complexes: Structures and Reactivities in the Solid State. *Coord. Chem. Rev.* **2003**, *237* (1–2), 183–196.
- (13) Woodall, C. H.; Beavers, C. M.; Christensen, J.; Hatcher, L. E.; Intissar, M.; Parlett, A.; Teat, S. J.; Reber, C.; Raithby, P. R. Hingeless Negative Linear Compression in the Mechanochromic Gold Complex [(C₆F₅Au)₂(μ-1,4-Diisocyanobenzene)]. *Angew. Chemie - Int. Ed.* **2013**, *52* (37), 9691–9694.
- (14) Seki, T.; Ozaki, T.; Okura, T.; Asakura, K.; Sakon, A.; Uekusa, H.; Ito, H. Interconvertible Multiple Photoluminescence Color of a Gold(I) Isocyanide Complex in the Solid State: Solvent-Induced Blue-Shifted and Mechano-Responsive Red-Shifted Photoluminescence. *Chem. Sci.* **2015**, *6* (4), 2187–2195.
- (15) Wong, K. M.; Yam, V. W. Self-Assembly of Luminescent Alkynylplatinum(II) Terpyridyl Complexes: Modulation of Photophysical Properties through Aggregation Behavior. *Acc. Chem. Res.* **2011**, *44* (6), 424–434.
- (16) Howlader, P.; Mondal, B.; Purba, P. C.; Zangrando, E.; Mukherjee, P. S. Self-Assembled Pd(II) Barrels as Containers for Transient Merocyanine Form and Reverse Thermochromism of Spiropyran. *J. Am. Chem. Soc.* **2018**, *140* (25), 7952–7960.
- (17) Brown, C. M.; Carta, V.; Wolf, M. O. Thermochromic Solid-State Emission of Dipyridyl Sulfoxide Cu(I) Complexes. *Chem. Mater.* **2018**, *30* (16), 5786–5795.
- (18) Boixel, J.; Guerchais, V.; Le Bozec, H.; Jacquemin, D.; Amar, A.; Boucekkine, A.; Colombo, A.; Dragonetti, C.; Marinotto, D.; Roberto, D.; et al. Second-Order NLO Switches from Molecules to Polymer Films Based on Photochromic Cyclometalated Platinum(II) Complexes. *J. Am. Chem. Soc.* **2014**, *136* (14), 5367–5375.
- (19) Cordones, A. A.; Lee, J. H.; Hong, K.; Cho, H.; Garg, K.; Boggio-Pasqua, M.; Rack, J. J.; Huse, N.; Schoenlein, R. W.; Kim, T. K. Transient Metal-Centered States Mediate Isomerization of a Photochromic Ruthenium-Sulfoxide Complex. *Nat. Commun.* **2018**, *9* (1).
- (20) Cariati, E.; Lucenti, E.; Botta, C.; Giovanella, U.; Marinotto, D.; Righetto, S. Cu(I) Hybrid Inorganic-Organic

Materials with Intriguing Stimuli Responsive and Optoelectronic Properties. *Coord. Chem. Rev.* **2016**, *306*, 566–614.

- (21) Wu, C.; Bull, B.; Christensen, K.; McNeill, J. Ratiometric Single-Nanoparticle Oxygen Sensors for Biological Imaging. *Angew. Chemie - Int. Ed.* **2009**, *48* (15), 2741–2745.
- (22) Yoshihara, T.; Yamaguchi, Y.; Hosaka, M.; Takeuchi, T.; Tobita, S. Ratiometric Molecular Sensor for Monitoring Oxygen Levels in Living Cells. *Angew. Chemie - Int. Ed.* **2012**, *51* (17), 4148–4151.
- (23) Komatsu, H.; Yoshihara, K.; Yamada, H.; Kimura, Y.; Son, A.; Nishimoto, S. I.; Tanabe, K. Ruthenium Complexes with Hydrophobic Ligands That Are Key Factors for the Optical Imaging of Physiological Hypoxia. *Chem. - A Eur. J.* **2013**, *19* (6), 1971–1977.
- (24) Visbal, R.; Gimeno, M. C. N-Heterocyclic Carbene Metal Complexes: Photoluminescence and Applications. *Chem. Soc. Rev.* **2014**, *43* (10), 3551–3574.
- (25) Fan, C.; Yang, C. Yellow/Orange Emissive Heavy-Metal Complexes as Phosphors in Monochromatic and White Organic Light-Emitting Devices. *Chem. Soc. Rev.* **2014**, *43* (17), 6439–6469.
- (26) Schmidt, R. Photosensitized Generation of Singlet Oxygen. *Photochem. Photobiol.* **2007**, *82* (5), 1161–1177.
- (27) Adachi, C.; Baldo, M. A.; Thompson, M. E.; Forrest, S. R. Nearly 100% Internal Phosphorescence Efficiency in an Organic Light Emitting Device. *J. Appl. Phys.* **2001**, *90* (10), 5048–5051.
- (28) Hasegawa, Y.; Nakagawa, T.; Kawai, T. Recent Progress of Luminescent Metal Complexes with Photochromic Units. *Coord. Chem. Rev.* **2010**, *254* (21–22), 2643–2651.
- (29) Aulsebrook, M. L.; Graham, B.; Grace, M. R.; Tuck, K. L. Lanthanide Complexes for Luminescence-Based Sensing of Low Molecular Weight Analytes. *Coord. Chem. Rev.* **2018**, *375*, 191–220.
- (30) Eber, G.; Grüneis, S.; Schneider, S.; Dörr, F. Dual Fluorescence Emission of Azulene Derivatives in Solution. *Chem. Phys Lett.* **1974**, *29*, 397–404.
- (31) Samanta, S.; Roy, M. B.; Chatterjee, M.; Ghosh, S. Simultaneous Emissions from T₂ and T₁ States of Naphthalene Moiety in a Specially Designed Naphthalene Cryptand. *J. Lumin.* **2007**, *126* (1), 230–238.
- (32) Gale, P. A.; Caltagirone, C. Anion Sensing by Small Molecules and Molecular Ensembles. *Chem. Soc. Rev.* **2015**, *44* (13), 4212–4227.

- (33) Han, J.; Loudet, A.; Barhoumi, R.; Burghardt, R. C.; Burgess, K. A Ratiometric PH Reporter for Imaging Protein-Dye Conjugates in Living Cells. *J. Am. Chem. Soc.* **2009**, *131* (5), 1642–1643.
- (34) Zhou, C.; Zhang, S.; Gao, Y.; Liu, H.; Shan, T.; Liang, X.; Yang, B.; Ma, Y. Ternary Emission of Fluorescence and Dual Phosphorescence at Room Temperature: A Single-Molecule White Light Emitter Based on Pure Organic Aza-Aromatic Material. *Adv. Funct. Mater.* **2018**, *28* (32), 1802407–1802412.
- (35) Matsushita, T.; Asada, T.; Koseki, S. Relativistic Study on Emission Mechanism in Palladium and Platinum Complexes. *J. Phys. Chem. A* **2006**, *110* (49), 13295–13302.
- (36) Baková, R.; Chergui, M.; Daniel, C.; Vlček Jr., A.; Zális, S. Relativistic Effects in Spectroscopy and Photophysics of Heavy-Metal Complexes Illustrated by Spin–orbit Calculations of $[\text{Re}(\text{Imidazole})(\text{CO})_3(\text{Phen})]^+$. *Coord. Chem. Rev.* **2011**, *255* (7–8), 975–989.
- (37) Escudero, D.; Thiel, W. Exploring the Triplet Excited State Potential Energy Surfaces of a Cyclometalated Pt(II) Complex: Is There Non-Kasha Emissive Behavior? *Inorg. Chem.* **2014**, *53* (20), 11015–11019.
- (38) Daniel, C. Photochemistry and Photophysics of Transition Metal Complexes: Quantum Chemistry. *Coord. Chem. Rev.* **2015**, *282–283*, 19–32.
- (39) Zhang, X.; Jacquemin, D.; Peng, Q.; Shuai, Z.; Escudero, D. General Approach to Compute Phosphorescent OLED Efficiency. *J. Phys. Chem. C* **2018**, *122* (11), 6340–6347.
- (40) Luo, Y.; Fu, C.; Chen, Z.; Hu, J.; Xu, Z.; Tang, D. Influence of Restricted Rotation of Small-Sized Substituent on Phosphorescence Efficiency for Pt(II) Complexes: A Theoretical Investigation. *Org. Electron. physics, Mater. Appl.* **2018**, *61*, 25–34.
- (41) Moitra, T.; Alam, M. M.; Chakrabarti, S. Intersystem Crossing Rate Dependent Dual Emission and Phosphorescence from Cyclometalated Platinum Complexes: A Second Order Cumulant Expansion Based Approach. *Phys. Chem. Chem. Phys.* **2018**, *20* (36), 23244–23251.

Chapter 2: Time-Dependent Density Functional Theory Study on Higher Low-Lying Excited States of $\text{Au}_{25}(\text{SR})_{18}^-$

2.1. Introduction

Gold clusters stabilized by organic molecules have attracted much attention owing to their molecule-like physicochemical properties, which depend on the metal core and/or surface ligand, unlike their bulk counterparts (e.g., photoluminescence,^{1–9} superatomic molecular orbitals,^{10–17} molecular chirality,^{18–20} catalyst^{21–24} and magnetism^{25–27}). The most extensively studied system is $[\text{Au}_{25}(\text{SR})_{18}]^-$, which is composed of an icosahedral Au_{13} core and six gold-thiolate complexes of $\text{Au}_2(\text{SR})_3$, hereafter called staples.^{28–30} The superatom view successfully explains its physical properties, which include high stability.¹² In $[\text{Au}_{25}(\text{SR})_{18}]^-$, eight of the thirteen 6s electrons of Au atoms in the metal core delocalize to form $1\text{S}^21\text{P}^61\text{D}^0$ superatomic shell closing, where the energy levels of the other 6s electrons are trapped to form $\text{Au}_{13}\text{-S}$ bonds and LUMO orbitals of D shell are split by the staple ligand field.^{31,32}

The photophysics of $[\text{Au}_{25}(\text{SR})_{18}]^-$ has attracted much interest for more than a decade.^{33–42} Studies on the optical properties have expanded to determine the effects of the surface charge,⁴³ oxidation state of metal core,⁴⁴ atomic composition,^{45–50} as well as the surface ligands, especially on the emission intensity.⁵¹ The luminescence of $[\text{Au}_{25}(\text{SR})_{18}]^-$ were reported to have peaks in the range 1–1.8 eV and around 2.5 eV as well summarized by Aikens *et al.*⁵² Among others, I in this study focus on representative three types of emissions whose peaks are around 1.1, 1.55, and 2.48 eV, with somewhat minor effects from the surface ligand. For instance, $[\text{Au}_{25}(\text{SG})_{18}]^-$ (SG = Glutathione) shows a dual emission with different emission lifetimes: a fast ns and slow μs .⁵³ The emission energies are around 1.1 eV (1100 nm) and 1.55 eV (800 nm) when the cluster is excited by a photon with 514 nm. The proposed mechanisms of these emissions are sp-intraband and sp-d interband transitions, where it is also not totally concluded whether the transitions occur from a triplet state or from a singlet state.⁵³ Ramakrishna et al. observed fluorescence at 1.49 eV (830 nm) for $[\text{Au}_{25}(\text{SC}_6\text{H}_{13})_{18}]^-$ by using two-photon excitation with a 1290-nm laser, and at 2.48 eV (500 nm) with an 800-nm laser.^{54,55} They propose that a visible emission is ascribed to the transition from the HOMO band

to the LUMO+1 band in the Au₁₃ core, and a near infrared one is related to the surface states that interact with the Au₁₃ core.^{56–58} Experiments were carried out to determine the relaxation dynamics in the excited state, reporting the ultrafast relaxation within the Au₁₃ core and slower relaxation concerning the Au-S semirings.^{42,59,60} It has recently been reported that the relaxation dynamics following sp-d interband transitions are different from sp-intraband transitions, and it is proposed that a near infrared emission results from the charge-transfer process that is mediated by the surface ligands.⁶¹

A recent theoretical study on the excited states of [Au₂₅(SR)₁₈][−] (R = H, Me, Et, Pr) attributed the origin of the near-infrared emission to the S₁ state that is mainly localized on the Au₁₃ core.⁵² By changing the ligand from H to alkyl ligand, the HOMO and LUMO bands are destabilized by 0.5–0.6 eV. In the case of the propylthiolated ligand (Pr), the large Stokes shift is caused by the largest geometrical changes in the S₁ state, unlike other ligands (R = H, Me, Et).⁵² Recent quantum dynamics studies for non-radiative excited state relaxation of [Au₂₅(SH)₁₈][−] showed fast relaxations from the higher states to S₇ and within the S₁–S₆ states,⁶² and the relaxation from the LUMO and LUMO+1 to HOMO is slower than other relaxation processes that are mediated by Au-Au and Au-S stretchings, respectively.⁶³ The S₇ state was found to have a distinctively long lifetime, and it is proposed that between the S₆ and S₇ states, there is a large energy gap whose detailed nature remains to be studied.⁶² It should be noted that in that non-radiative dynamics study, the nuclear motion of the gold cluster is obtained by the ground state molecular dynamics under the classical path approximation, although the results are suggestive. From these studies, the origin of the near infrared emission (~1.1 eV) and the geometrical changes in the excited states were revealed. To enhance my understanding of the [Au₂₅(SR)₁₈][−], higher excited states should be explored for higher-energy emissions that are centered around 1.55 and 2.48 eV.

In this study, I calculated the higher low-lying excited states of [Au₂₅(SR)₁₈][−] (R = Me, EtPh) to gain further insights into the multiple-emission mechanism. In particular, I focused on the S₇ state, as it is believed to have a distinctively long lifetime.

2.2. Computational Details

All the ground and excited-state structures were optimized in gas phase using the density functional theory (DFT) and time-dependent DFT (TD-DFT) calculations, as implemented in Turbomole package 7.0.1 ~ 7.1.⁶⁴ The PBE⁶⁵ or B3LYP⁶⁶⁻⁶⁸ exchange-correlation functional, the def-SV(P) basis set with a default 60-electron relativistic effective core potentials for Au,⁶⁹ and the Resolution of Identity approximation were used. The use of CAM-B3LYP⁷⁰/def2-SVP⁷¹, as implemented in Gaussian 09,⁷² overestimated the experimental excitation energies by ~0.3 eV. The theoretical models are based on $[\text{NOct}_4]^+[\text{Au}_{25}(\text{SEtPh})_{18}]^-$ (Oct: octyl), where I studied the ground and excited states of $[\text{Au}_{25}(\text{SMe})_{18}]^-$ and $[\text{Au}_{25}(\text{SEtPh})_{18}]^-$ without counter cations. The vibration analyses carried out with PBE and B3LYP for the optimized structures in the ground state show that $[\text{Au}_{25}(\text{SMe})_{18}]^-$ has all real-number frequencies (minimum), whereas $[\text{Au}_{25}(\text{SEtPh})_{18}]^-$ has two imaginary-number frequencies ($9.69i$, $1.92i \text{ cm}^{-1}$) with PBE (although their magnitudes are negligibly small). For absorption spectra, the line spectra obtained by the TDDFT calculations were convoluted by a Lorentzian of width 10 nm. All structures and molecular orbitals were visualized by using the VESTA 2.1.6.⁷³

2.3. Results and Discussion

2.3.1. Comparison between Different Models and Functionals

First, I study the difference in the structural and electronic properties of $[\text{Au}_{25}(\text{SMe})_{18}]^-$ with B3LYP and PBE and $[\text{Au}_{25}(\text{SEtPh})_{18}]^-$ with PBE at their ground state geometry. Differences in the bond distances in the ground state structures are small (see Table S7). The electronic structures calculated with B3LYP and PBE are similar and the frontier orbitals are quasi-degenerate. The nature of frontier orbitals from HOMO-2 to LUMO+4 are almost unchanged by substituting protecting ligands because these orbitals are mainly localized around the Au_{13} core, as well as by employing the different functionals. From the superatom perspective, HOMO-2 to HOMO are triply degenerate P orbitals, LUMO and LUMO+1 are assigned to D_{z^2} and $D_{x^2-y^2}$, respectively, and LUMO+2 to LUMO+4 are assigned to $D_{xy/yz/zx}$ orbitals, where the D orbitals are shown to split in energy owing to the six protecting Au-S staple ligands, as discussed in the next section. These superatomic orbitals mostly consist of Au 6s atomic orbitals,

and the Au 5d band is found between superatomic S and P orbitals.

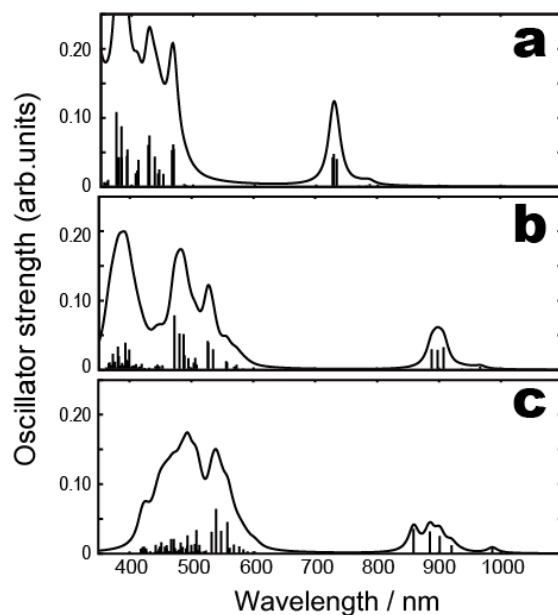


Figure 1. Simulated absorption spectra up to 200 states of a) $[\text{Au}_{25}(\text{SMe})_{18}]^-$ with B3LYP, b) $[\text{Au}_{25}(\text{SMe})_{18}]^-$ with PBE, and c) $[\text{Au}_{25}(\text{SEtPh})_{18}]^-$ with PBE.

Figure 1 compares the calculated absorption spectra of $[\text{Au}_{25}(\text{SMe})_{18}]^-$ with B3LYP and PBE, and those of $[\text{Au}_{25}(\text{SEtPh})_{18}]^-$ with that of PBE. The lowest energy-absorption peak is observed at 1.38 eV with PBE and 1.70 eV with B3LYP in $[\text{Au}_{25}(\text{SMe})_{18}]^-$. The use of B3LYP gives a better agreement with the experimental value of 1.85 eV⁷⁴ than the use of PBE (< 0.2 eV) with the higher computational costs. Although there are quantitative differences in their excitation energies, I confirm that they are qualitatively the same among different surface ligands and functionals used, as reported earlier.⁵² As shown in Figure 1a–1c, all the lowest energy absorption peaks consist of $S_1 \sim S_6$, and the energy gaps between S_6 and S_7 are large. The $S_1 \sim S_6$ states are assigned to the Au 6sp intraband transition having a $P \rightarrow D_{z^2/x^2-y^2}$ transition nature, whereas S_7 and higher are assigned to the Au 6sp intraband transition from P to $D_{xy/yz/zx}$, as well as 5d-6sp interband transitions assigned to 5d to D orbitals. This is summarized in Tables S1 to S3.

I discuss differences between the molecular models. HOMO-2 to HOMO of $[\text{Au}_{25}(\text{SMe})_{18}]^-$ are quasi-degenerate within 0.03 eV, and within 0.06 eV for $[\text{Au}_{25}(\text{SEtPh})_{18}]^-$. The absorption spectrum of $[\text{Au}_{25}(\text{SEtPh})_{18}]^-$ shows a larger split in peaks around 900 nm compared to the relatively sharp peak of $[\text{Au}_{25}(\text{SMe})_{18}]^-$. The split is due to the lower symmetry in the core, which is caused by the bulky ligands of $[\text{Au}_{25}(\text{SEtPh})_{18}]^-$. In addition, the orbital energies of $[\text{Au}_{25}(\text{SEtPh})_{18}]^-$ are lower than those of $[\text{Au}_{25}(\text{SMe})_{18}]^-$, which is consistent with a previous report.⁷⁵ The stabilization

in $[\text{Au}_{25}(\text{SEtPh})_{18}]^-$ can partly originate from intramolecular interactions such as Au-H hydrogen bonding interaction, as reported recently for phosphine protecting gold clusters.⁷⁶ The $S_1 \sim S_6$ states of $[\text{Au}_{25}(\text{SMe})_{18}]^-$ are independent of the functionals used. Although the S_7 state at the ground state geometry calculated with PBE has a different nature from that with B3LYP, similar electronic states can be found. The S_8 state obtained with PBE is similar to the S_7 state obtained with B3LYP, and the S_7 and S_8 states are quasi-degenerate (see Tables S1 and S2). The difference between PBE and B3LYP may be related to the optimized bond distances. However, I can safely ignore the different characteristics of the PBE and B3LYP calculations because two S_7 minimum structures are observed with both the functionals having very similar energies. I discuss this in detail in section 3.4.

Because the calculated absorption spectra are qualitatively independent of the surface ligand and functionals used, hereafter, I focus on the excited state of $[\text{Au}_{25}(\text{SMe})_{18}]^-$ calculated with B3LYP. In the following subsection, all the results are those calculated by B3LYP, unless otherwise noted.

2.3.2. Ligand Field Splitting of Superautom D Orbitals

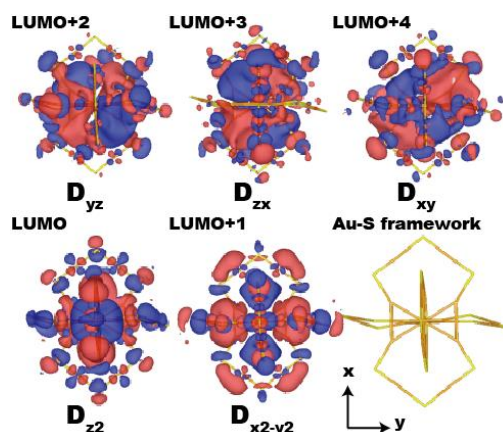


Figure 2. LUMO ~ LUMO+4 of $[\text{Au}_{25}(\text{SMe})_{18}]^-$ from the view shown in the right bottom as Au-S framework.

Here, I focus on the splitting of D orbitals. The doubly degenerate LUMO and LUMO+1 have D_{z^2} and $D_{x^2-y^2}$ (e_g) characteristics, and triply degenerate LUMO+2 to LUMO+4 have D_{xy} , D_{yz} and D_{zx} (t_{2g}) features (see Figure 2), as

reported previously.³¹ The splitting is interesting and unfamiliar because six-coordinated octahedral complexes have lower t_{2g} and higher e_g orbitals,⁷⁷ as opposed to the present case. Aikens et al. reproduced the ligand field splitting by using an electrostatic model that mimic the staple ligands in an ideal way, which gives a tetrahedral (T_h) symmetry,³² where the e orbitals are energetically lower than t_2 orbitals⁷⁷. Here, to add a few words, I consider the V shape of the staple. Although the e_g - t_{2g} splitting was previously ascribed to the V shape of the staples, the reason was not clearly explained.³¹ In the present Au_{25} clusters, the lobes of D_{xy} , D_{yz} and D_{zx} point toward the bonding direction of the $Au_2(SR)_3$ ligands, unlike D_{z^2} and $D_{x^2-y^2}$. In short, D_{xy} , D_{yz} and D_{zx} experience stronger electrostatic repulsions than D_{z^2} and $D_{x^2-y^2}$, whose lobes are located in the vacancy of the staple ligands with the weaker electrostatic repulsions owing to the V-shape ligands. Thus these electrostatic repulsions are the opposite of conventional six-coordinated mononuclear octahedral complexes.

2.3.3. Analysis of Absorption Spectrum as Spherical Harmonics

In Figure 1, the lowest-lying peaks are $S_1 \sim S_6$, where the oscillator strengths of $S_1 \sim S_3$ are weaker than those of $S_4 \sim S_6$. To obtain more insights into the oscillator strength for $S_1 \sim S_6$, I analyzed the transition moments using the spherical harmonics. There are six possible transitions from triply degenerate P to doubly degenerate D orbitals; $\langle P_i | \vec{\mu} | D_j \rangle$ ($i = x, y, z$; $j = z^2, x^2 - y^2$), where $\vec{\mu} = (x, y, z)$ is a dipole moment in the atomic unit. The transition moments for the excited states (not the orbital) can then be expressed by the linear combination of these orbital transition moments, which can be estimated using the spherical harmonics as follows.

$$\langle n' l' m' | x | n l m \rangle = \int_0^R \int_0^\pi \int_0^{2\pi} \Psi_{n', l', m'}^*(r, \theta, \varphi) x \Psi_{n, l, m}(r, \theta, \varphi) r^2 \sin \theta dr d\theta d\varphi$$

$$\Psi_{n, l, m} = R_{n, l} Y_{l, m}$$

Hence, $R_{n, l}$ and $Y_{l, m}$ are the normalized radial wavefunction and spherical harmonics, respectively, with quantum numbers (n, l, m) , where n is the principal, l is the azimuthal ($l = 1$ is a P orbital, $l = 2$ is a D orbital), and m is the magnetic quantum numbers. The integral is evaluated for x, y , and z as an operator. The ratio of these transition dipole moments is shown in Table S4 in Supporting Information for the following expressions:

$$P_x = x f_1(r), P_y = y f_1(r), P_z = z f_1(r)$$

$$D_{x^2-y^2} = \frac{1}{2}(x^2 - y^2)f_2(r), D_{z^2} = \frac{\sqrt{3}}{2}(3z^2 - r^2)f_2(r)$$

Table S4 shows that $\langle P_x|x|D_{z^2} \rangle$, $\langle P_y|y|D_{z^2} \rangle$, $\langle P_x|x|D_{x^2-y^2} \rangle$, $\langle P_y|y|D_{x^2-y^2} \rangle$, and $\langle P_z|z|D_{z^2} \rangle$ are nonzero transition dipole moments. It should be noted that if I consider the real structure of orbitals such that $[\text{Au}_{25}(\text{SR})_{18}]^-$ is not a complete spherical structure, P_x , P_y and P_z orbitals are not rigorously orthogonal, and P_x and P_y are not in the axial direction of $D_{x^2-y^2}$. Among others, $\langle P_z|z|D_{z^2} \rangle$ is distinctively large, which is included in transitions to the $S_4 \sim S_6$ states. This may be a reason for the large oscillator strength of the $S_4 \sim S_6$ states compared to the $S_1 \sim S_3$ states.

2.3.4. Electronics Excited States

Below, I will discuss the electronic excited states to understand the multiple photoluminescence values of the Au_{25} clusters. I start a discussion by the minimum structure in the S_1 state ($S_{1\text{MIN}}$) on the basis of the well-known Kasha's rule⁷⁸, which states that a photoluminescence generally occurs from the lowest excited state. The emission energy for the S_1 state at $S_{1\text{MIN}}$ was found to be 0.88 eV (1409 nm) where the main character is an excitation from HOMO (P) to LUMO (D), which is the Au sp intraband transition. Considering the underestimation of the absorption energy by 0.15 eV in the ground state, the emission energy is estimated to be 1.03 eV (1204 nm), which is very close to the experimental value of 1.1 eV. However, the emission energy for an optimized T_1 state is calculated to be 0.70 eV (1771 nm), which is too small compared to the experimental value, even after correcting for the underestimation. This result is in agreement with a recent theoretical report.⁵²

The excitation energies differ substantially between S_6 and S_7 states (0.75 eV), as can be seen in the absorption spectrum (Figure 1), indicating that emissions with higher energies may occur from the S_7 state, competing with the internal conversions in the cases such as azulene.⁷⁹ I have obtained two different structures in the S_7 state after extensive geometry optimization searches. The one with the lower energy (which is denoted by $S_{7\text{MIN}}^{\text{non}}$) is mainly characterized as an intraband transition from HOMO-2 (P) to LUMO+1 (D), where the energy difference from the S_0 state is 1.85 eV; however, it is energetically very close to the S_6 state, indicating a fast internal conversion, and is therefore nonemissive. The other one (which is denoted by $S_{7\text{MIN}}^{\text{em}}$) is characterized mainly by an interband transition

from HOMO-3 (Au 5d, S 3p) to LUMO (D), where the energy difference from its S_0 state is 2.19 eV. Unlike the $S_{7\text{MIN}}^{\text{non}}$, the energy gap between S_6 and S_7 states is 0.46 eV at the $S_{7\text{MIN}}^{\text{em}}$ structure, indicating a slower internal conversion than at the $S_{7\text{MIN}}^{\text{non}}$ structure. This $S_{7\text{MIN}}^{\text{em}}$ structure may be the reason for the slow relaxation from the S_7 to S_6 state found in the previous molecular dynamics study on $[\text{Au}_{25}(\text{SH})_{18}]^-$.⁶² The emission energy from the $S_{7\text{MIN}}^{\text{em}}$ structure is estimated to be 2.34 eV (530 nm) by correcting the underestimation of 0.15 eV. This value is in good agreement with the experimental value of 2.48 eV (Table 1). The two minima in the S_7 state are found in both PBE and B3LYP calculations.

To determine the origin of the emission at 1.55 eV, I further carried out geometry optimizations in the respective $S_2 \sim S_6$ states. Some optimizations failed because of the quasi-degeneracy of the excited states, indicating the existence of a conical intersection nearby. It is turned out that these states are nonemissive because their energies are very close to the lower states (Table S6). The geometry optimization, starting from $S_{7\text{MIN}}^{\text{non}}$ to $S_{1\text{MIN}}$, did not identify any emissive structures. However, the emission energy from the S_4 state is 1.47 eV after correcting for the underestimation, which is close to 1.55 eV, although there is no energy gap with S_3 . Changes in the surface ligands may further stabilize the S_4 state, opening a gap. Another possibility is be the spin-orbit coupling effects for the splitting of S_1 or S_7 , or other states.⁴⁰

Table 1. Raw and estimated emission energies obtained by the TDDFT calculation for the $S_{1\text{MIN}}$, $S_{4\text{MIN}}$, and $S_{7\text{MIN}}^{\text{em}}$ states of $[\text{Au}_{25}(\text{SMe})_{18}]^-$, as well as the experimental emission energies. The estimation is performed by adding an underestimation of 0.15 eV to the calculated raw values.

	Emission energy / eV		
	S_1	S_4	S_7
Raw	0.88 (1409 nm)	1.32 (939 nm)	2.19 (566 nm)
Estimated	1.03 (1204 nm)	1.47 (844 nm)	2.34 (530 nm)
Experimental	1.1 (1127 nm) ⁵³	1.55 (800 nm) ⁵³	2.48 (500 nm) ^{46,48}

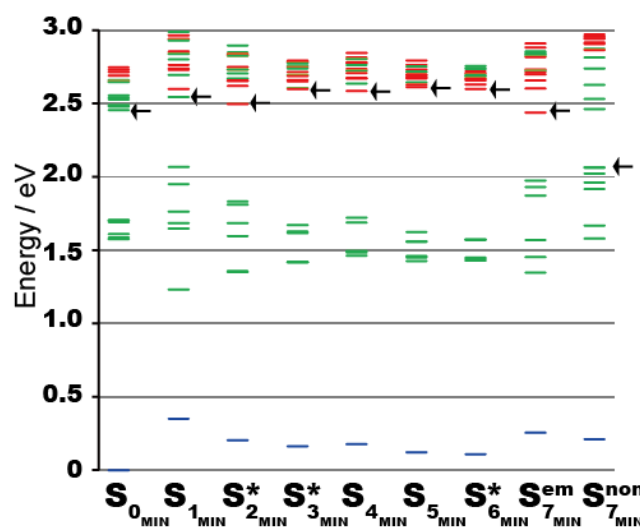


Figure 3. Relative energies of the ground and low-lying excited state of $[\text{Au}_{25}(\text{SMe})_{18}]^-$ at the optimized structures in the respective $S_0 \sim S_7$ states. Up to 20 excited states are shown. The zero represents the ground state energy. Blue, green, and red bars show the ground state, intraband, and interband, respectively. The arrows show the S_7 excited state for each structure. The asterisk represents a snapshot because the optimization is not fully converged.

Figure 3 classifies the excited states at each optimized structure, where green and red bars denote intraband and interband transitions, respectively. Some structures could not be fully optimized because their energies are very close to the lower states and these states are shown with an asterisk in Figures 3-5. The S_1 – S_6 states for all the optimized structures are characterized by the intraband transition. The S_7 state of $S_{0\text{MIN}}$, $S_{1\text{MIN}}$ and $S_{7\text{MIN}}^{\text{non}}$ represents the intraband transition, while the S_7 state of the $S_{2\text{MIN}} \sim S_{7\text{MIN}}^{\text{em}}$ structures represents the interband transition. At the $S_{1\text{MIN}}$ structure, the interband transition is found in the S_8 state, which is energetically close to the S_7 state.

Because the excited states lying higher than S_7 are somewhat dense, a very small structural difference easily alters the excited states with different characters, namely the intra- and inter-band transitions, as well as the oscillator strengths. Compared to the S_7 state, the S_1 state is robust and stable because the quasi-degenerate S_1 - S_6 states share the similar characteristics. Even if I optimize the S_1 state starting from different initial structures (Table S5), its characteristics and emission energy are almost the same.

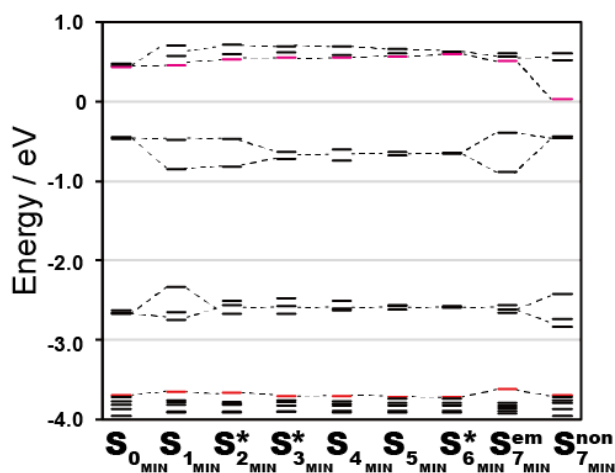


Figure 4. Orbital energies from HOMO-8 to LUMO+4 at each optimized structure. HOMOs and LUMOs are below and above the -2.0 eV. Red and pink bars highlight HOMO-3 and LUMO+2, respectively. The asterisk represents a snapshot because the geometry optimization was not fully converged.

Figure 4 summarizes the orbital energies of $S_{0\text{MIN}}$ to $S_{7\text{MIN}}^{\text{non}}$ structures. The amounts of energy splitting in quasi-degenerate HOMOs and LUMOs may be a measure of the structural distortion in the Au_{13} core following the structural relaxation for each electronic transition. The splitting in the quasi degenerate orbital energies for the S_1 states is in good agreement with the Aikens's result.⁵² Higher low-lying excited states for $S_{3\text{MIN}} \sim S_{6\text{MIN}}$ have fewer splits. Splits in the orbital energies in the two S_7 states are different, depending on their electronic transitions. The nature of electronic structure at $S_{7\text{MIN}}^{\text{em}}$ is a $\text{Au}(d)$ to $\text{D}(e_g)$ transition, and therefore, the P orbitals (HOMOs) still appear to be well degenerate, while LUMO and LUMO+1 split largely. On the other hand, the $S_{7\text{MIN}}^{\text{non}}$ is optimized for a $\text{P-D}(t_{2g})$ transition, and thus the splits in P and $\text{D}(t_{2g})$ orbitals are large.

Figure 5 depicts the bond distances for Au-Au and Au-S. The variation in the pattern of bond distances is closely correlated with the orbital energy diagram because the structural distortions in the Au_{13} core are governed by the quasi-degenerate frontier orbitals. The larger the splitting in the orbital energies is, the larger the distortion in its Au_{13} core structure is. The Au-S bond distances are relatively inert compared to the dynamical changes in the Au_{13} core.

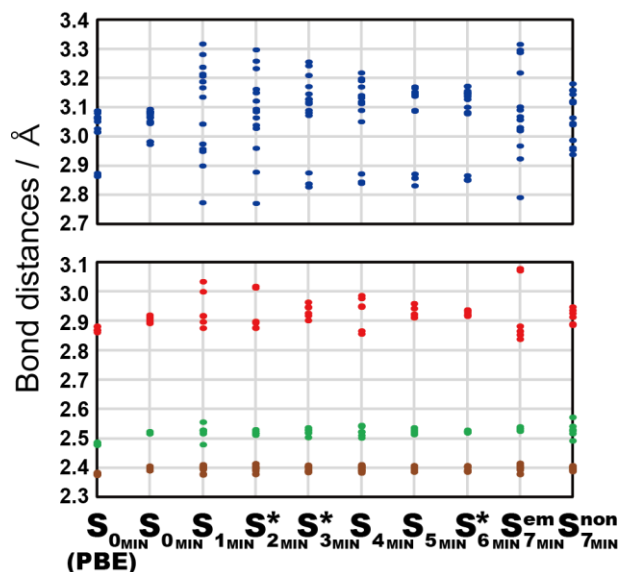


Figure 5. Bond distances of optimized structures in the ground and excited states of $[\text{Au}_{25}(\text{SMe})_{18}]^-$. Blue, red, green, and brown dots show $\text{Au}^s\text{-Au}^s$, $\text{Au}^c\text{-Au}^s$, $\text{Au}^s\text{-S}$, and Au-S in Au-S staple, respectively. See Table 2 for the abbreviations. The asterisk represents a snapshot because the optimization is not fully converged.

Here, I briefly discuss the differences between PBE and B3LYP. As shown in Figure 5, the $\text{Au}^s\text{-Au}^s$ distances at $\text{S}_{0\text{MIN}}$ are shorter with PBE (~ 0.11 Å) than with B3LYP. Previous studies reported that the Au-Au distances can vary depending on functionals in DFT.⁸⁰⁻⁸⁵ Comparing the electronic structures of $\text{S}_{0\text{MIN}}$ of $[\text{Au}_{25}(\text{SMe})_{18}]^-$ optimized with PBE and B3LYP, the energy gap between the Au-5d band and HOMOs (Au-6sp) is 0.3 eV smaller for PBE. The smaller 5d-6s energy gap can enhance the mixing of the 5d and 6s electrons, which is known to be the origin of the aurophilic interactions. As discussed above, the small structural difference can vary the order of the S_7 and higher excited states, causing different S_7 characters to be obtained at the ground state geometries (Table S1 and S2). Although there are quantitative differences in the higher excited states, I also found two $\text{S}_{7\text{MIN}}$, even with PBE, and therefore, the qualitative result and the overall discussion are unchanged in the present study.

Table 2 shows the average and standard deviation for the representative bond distances of $\text{S}_{0\text{MIN}}$, $\text{S}_{1\text{MIN}}$, and $\text{S}_{7\text{MIN}}^{\text{em}}$

of $[\text{Au}_{25}(\text{SMe})_{18}]^-$. The Au-Au and Au-S distances in S_0 are relatively uniform, with standard deviations of 0.010 and 0.003 Å, respectively. In $S_{1\text{MIN}}$, the Au_{13} cores take a prolate-like structure. Analyses of the molecular orbitals reveals that the direction of the elongation is related to the direction of the lobes of anti-bonding orbitals. The structural distortion of $S_{1\text{MIN}}$ is larger than that of $S_{7\text{MIN}}^{\text{em}}$. This is related to the magnitude of the Stokes shift, which is 0.69 eV in $S_{1\text{MIN}}$ and 0.27 eV in $S_{7\text{MIN}}^{\text{em}}$ (Table 3). This difference is correlated with the large energy separation between the S_7 and S_6 states in $S_{7\text{MIN}}^{\text{em}}$ as in $S_{0\text{MIN}}$. The smaller the change in geometry is, the closer the excited state to that obtained in the ground state is.

Table 2 Averaged values and standard deviation of Au-Au and Au-S bond distances for $S_{0\text{MIN}}$, $S_{1\text{MIN}}$, and $S_{7\text{MIN}}^{\text{em}}$ of $[\text{Au}_{25}(\text{SMe})_{18}]^-$. Au^c and Au^s represent the center and surface Au atoms of the Au_{13} core.

	$\text{Au}^c - \text{Au}^s / \text{\AA}$	$\text{Au}^s - \text{S} / \text{\AA}$
$S_{0\text{MIN}}$	2.903 ± 0.010	2.518 ± 0.003
$S_{1\text{MIN}}$	2.939 ± 0.057	2.521 ± 0.023
$S_{7\text{MIN}}^{\text{em}}$	2.929 ± 0.102	2.531 ± 0.005

Table 3 Stokes shifts in $S_{1\text{MIN}}$ and $S_{7\text{MIN}}^{\text{em}}$

	$\lambda_{\text{ex.}} / \text{eV}$	$\lambda_{\text{em.}} / \text{eV}$	Stokes shift / eV
$S_{1\text{MIN}}$	1.57	0.88	0.69
$S_{7\text{MIN}}^{\text{em}}$	2.46	2.19	0.27

2.3.5. Energy Profiles between $S_{7\text{MIN}}^{\text{em}}$ and $S_{7\text{MIN}}^{\text{non}}$

Here, I discuss an energy barrier between the two S_7 minima. I calculated the energy profile for a path connecting the two minima in the S_7 state, $S_{7\text{MIN}}^{\text{em}}$ and $S_{7\text{MIN}}^{\text{non}}$. The structures between the two minima in the S_7 state are obtained using the linear interpolation without any further geometry optimizations. The result is shown in Figure 6. Twelve structures are used to interpolate the two S_7 minima in the S_7 state. Along these geometries, I found energy barrier from $S_{7\text{MIN}}^{\text{em}}$ to $S_{7\text{MIN}}^{\text{non}}$ is 0.06 eV; in contrast, it is 0.43 eV from $S_{7\text{MIN}}^{\text{non}}$ to $S_{7\text{MIN}}^{\text{em}}$. This energy barrier can be interpreted as an upper bound for the activation energy between the two S_7 minima if one could obtain the transition state and the intrinsic reaction coordinate for this pathway. Although this small value indicates a fast

transition between $S_{7\text{MIN}}^{\text{em}}$ and $S_{7\text{MIN}}^{\text{non}}$, it may remain around the $S_{7\text{MIN}}^{\text{em}}$ structure if I consider dynamical effects⁶² and then emit the light from $S_{7\text{MIN}}^{\text{em}}$.

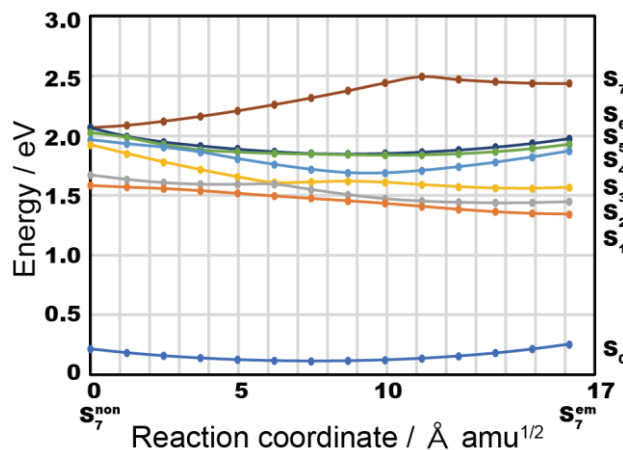


Figure 6. Energy profile along the linearly interpolated geometries between the two S_7 minima of $[\text{Au}_{25}(\text{SMe})_{18}]^-$.

2.3.6. Relaxation from S_{30} State of $\text{Au}_{25}(\text{SH})_{18}^-$

Ramakrishna et al. observed the two-photon excited emission at 2.48 eV when the cluster is excited at 800 nm (3.1 eV).^{54,55} To observe the relaxation pathway from a highly excited state, I examine the relaxation from the S_{30} state of $[\text{Au}_{25}(\text{SH})_{18}]^-$ under the C_i symmetry using the PBE functional because this state has a relatively strong oscillator strength (2.67 eV, $f = 9.41 \times 10^{-2}$), where the excitation energy will be 3.03 eV after correcting for the underestimation that is larger with PBE than with B3LYP. I also found two types of S_7 states for $[\text{Au}_{25}(\text{SH})_{18}]^-$ with PBE. I expected that the gold cluster relaxes to the emissive S_7 state after being excited to the S_{30} state. It should be noted that during the step-by-step optimizations from S_{30} down to S_7 , some excited states were not fully optimized. In these states, the very small energy gap with the lower excited states hampers the full relaxation into a local minimum. Around these structures, I consider that the optimization reaches points that are very close to a conical intersection, then I moved to the optimization with the next lower excited state. During the relaxation, the maximum energy gap with the next lower excited state was 0.05 eV. Unfortunately, the relaxation results in the nonemissive S_7 state, i.e., a state that is energetically very close to S_6 , suggesting a fast internal conversion down to the S_1 state. For getting further insights

into the relaxation pathway, dynamical effects will be required to be considered as in the previous quantum dynamics study, which found the S_7 state having a long lifetime.⁶²

2.4. Concluding Remarks

DFT and TDDFT calculations have been carried out for gold-thiolate clusters, $[\text{Au}_{25}(\text{SR})_{18}]^-$ ($\text{R} = \text{Me}, \text{EtPh}$), in gas phase in order to obtain insights into the mechanism of multiple emissions at 1.55 and 2.48 eV. The excited states of the clusters are found to be independent of the surface ligands from the analysis of absorption spectra, enabling us to use the smaller model system of $[\text{Au}_{25}(\text{SMe})_{18}]^-$. I found two S_7 minima for $[\text{Au}_{25}(\text{SMe})_{18}]^-$, one of which ($S_{7\text{MIN}}^{\text{em}}$) is an interband transitions with a large energy gap from the lower excited states, and the other ($S_{7\text{MIN}}^{\text{non}}$) is an intraband transitions with a small energy gap. It is proposed that the emission at 2.48 eV is caused by the $S_{7\text{MIN}}^{\text{em}}$. To characterize the excited states, I performed structural and orbital analyses that focus on the Au_{13} core. An emissive state having an energy difference of 1.55 eV could not be determined, but the S_4 state was found to be a possible state. Further studies are being carried out to clarify the emission mechanism. In the future work, to fully elucidate the excited state behavior of the gold-thiolate clusters, the dynamical effects should be included, as well as the spin-orbit coupling effects.

2.5. Supporting Information

Table S1. Excitation energy, oscillator strength, and details of the transitions and their contributions for $[\text{Au}_{25}(\text{SMe})_{18}]^-$ obtained by TDDFT calculations with B3LYP. The transitions are shown in terms of the orbital number as well as the interpretations if possible from the superatom perspective; p^s is S (3p).

Excited state	Excitation energy / eV	Oscillator strength	Transitions	Contribution / %
S ₁	1.57	4.29×10^{-3}	HOMO $\rightarrow$ LUMO (P $\rightarrow$ D)	65.9
			HOMO-1 $\rightarrow$ LUMO (P $\rightarrow$ D)	13.7
			HOMO $\rightarrow$ LUMO+1 (P $\rightarrow$ D)	8.0
			HOMO-1 $\rightarrow$ LUMO+1 (P $\rightarrow$ D)	5.5
S ₂	1.59	2.05×10^{-3}	HOMO $\rightarrow$ LUMO+1 (P $\rightarrow$ D)	50.6
S ₃	1.61	1.91×10^{-3}	HOMO-1 $\rightarrow$ LUMO (P $\rightarrow$ D)	41.3
			HOMO-2 $\rightarrow$ LUMO+1 (P $\rightarrow$ D)	54.4
			HOMO-1 $\rightarrow$ LUMO (P $\rightarrow$ D)	25.2
			HOMO $\rightarrow$ LUMO+1 (P $\rightarrow$ D)	9.2
S ₄	1.69	4.04×10^{-2}	HOMO $\rightarrow$ LUMO (P $\rightarrow$ D)	6.1
			HOMO-2 $\rightarrow$ LUMO+1 (P $\rightarrow$ D)	28.1
			HOMO $\rightarrow$ LUMO (P $\rightarrow$ D)	19.0
			HOMO $\rightarrow$ LUMO+1 (P $\rightarrow$ D)	16.2
			HOMO-1 $\rightarrow$ LUMO (P $\rightarrow$ D)	12.7
			HOMO-2 $\rightarrow$ LUMO (P $\rightarrow$ D)	10.5
S ₅	1.70	4.75×10^{-2}	HOMO-1 $\rightarrow$ LUMO+1 (P $\rightarrow$ D)	10.2
			HOMO-1 $\rightarrow$ LUMO+1 (P $\rightarrow$ D)	43.4
			HOMO-2 $\rightarrow$ LUMO (P $\rightarrow$ D)	31.7
			HOMO-2 $\rightarrow$ LUMO+1 (P $\rightarrow$ D)	10.5
S ₆	1.71	4.30×10^{-2}	HOMO-1 $\rightarrow$ LUMO (P $\rightarrow$ D)	5.6
			HOMO-2 $\rightarrow$ LUMO (P $\rightarrow$ D)	42.9
			HOMO-1 $\rightarrow$ LUMO+1 (P $\rightarrow$ D)	35.2
			HOMO $\rightarrow$ LUMO+1 (P $\rightarrow$ D)	11.5
S ₇	2.46	8.13×10^{-4}	HOMO $\rightarrow$ LUMO (P $\rightarrow$ D)	4.3
			HOMO $\rightarrow$ LUMO+2 (P $\rightarrow$ D)	65.6
			HOMO-1 $\rightarrow$ LUMO+2 (P $\rightarrow$ D)	11.9
			HOMO-2 $\rightarrow$ LUMO+2 (P $\rightarrow$ D)	7.7
S ₈	2.48	9.15×10^{-4}	HOMO $\rightarrow$ LUMO+4 (P $\rightarrow$ D)	6.7
			HOMO $\rightarrow$ LUMO+3 (P $\rightarrow$ D)	33.9
			HOMO-1 $\rightarrow$ LUMO+3 (P $\rightarrow$ D)	27.3

S ₉	2.49	5.77×10^{-5}	HOMO-1 $\rightarrow$ LUMO+4 (P $\rightarrow$ D)	14.9
			HOMO-1 $\rightarrow$ LUMO+2 (P $\rightarrow$ D)	7.5
			HOMO-2 $\rightarrow$ LUMO+2 (P $\rightarrow$ D)	6.9
			HOMO-1 $\rightarrow$ LUMO+3 (P $\rightarrow$ D)	30.0
			HOMO-2 $\rightarrow$ LUMO+2 (P $\rightarrow$ D)	28.4
			HOMO $\rightarrow$ LUMO+4 (P $\rightarrow$ D)	20.8
			HOMO-2 $\rightarrow$ LUMO+3 (P $\rightarrow$ D)	6.2
S ₁₀	2.53	1.58×10^{-3}	HOMO $\rightarrow$ LUMO+2 (P $\rightarrow$ D)	5.6
			HOMO-1 $\rightarrow$ LUMO+2 (P $\rightarrow$ D)	31.7
			HOMO-2 $\rightarrow$ LUMO+3 (P $\rightarrow$ D)	23.6
			HOMO $\rightarrow$ LUMO+3 (P $\rightarrow$ D)	21.7
			HOMO $\rightarrow$ LUMO+4 (P $\rightarrow$ D)	12.0
S ₁₁	2.54	2.96×10^{-3}	HOMO $\rightarrow$ LUMO+2 (P $\rightarrow$ D)	3.6
			HOMO-1 $\rightarrow$ LUMO+3 (P $\rightarrow$ D)	26.6
			HOMO $\rightarrow$ LUMO+4 (P $\rightarrow$ D)	20.4
			HOMO-1 $\rightarrow$ LUMO+4 (P $\rightarrow$ D)	13.9
			HOMO-2 $\rightarrow$ LUMO+3 (P $\rightarrow$ D)	13.4
			HOMO $\rightarrow$ LUMO+2 (P $\rightarrow$ D)	6.9
			HOMO-2 $\rightarrow$ LUMO+2 (P $\rightarrow$ D)	5.3
S ₁₂	2.55	4.25×10^{-3}	HOMO $\rightarrow$ LUMO+3 (P $\rightarrow$ D)	4.2
			HOMO-2 $\rightarrow$ LUMO+4 (P $\rightarrow$ D)	57.5
			HOMO-1 $\rightarrow$ LUMO+2 (P $\rightarrow$ D)	11.5
			HOMO-2 $\rightarrow$ LUMO+2 (P $\rightarrow$ D)	10.8
			HOMO-1 $\rightarrow$ LUMO+3 (P $\rightarrow$ D)	5.5
			HOMO-2 $\rightarrow$ LUMO+3 (P $\rightarrow$ D)	5.1
			HOMO-1 $\rightarrow$ LUMO+2 (P $\rightarrow$ D)	22.4
S ₁₃	2.65	5.48×10^{-2}	HOMO-2 $\rightarrow$ LUMO+3 (P $\rightarrow$ D)	17.1
			HOMO-1 $\rightarrow$ LUMO+4 (P $\rightarrow$ D)	14.0
			HOMO-2 $\rightarrow$ LUMO+4 (P $\rightarrow$ D)	12.1
			HOMO $\rightarrow$ LUMO+2 (P $\rightarrow$ D)	8.5
			HOMO-5 $\rightarrow$ LUMO (d, p ^s $\rightarrow$ D)	7.4
			HOMO-6 $\rightarrow$ LUMO+1 (d, p ^s $\rightarrow$ D)	4.3
			HOMO-7 $\rightarrow$ LUMO+1 (d, p ^s $\rightarrow$ D)	3.4
S ₁₄	2.65	3.25×10^{-6}	HOMO-2 $\rightarrow$ LUMO+2 (P $\rightarrow$ D)	2.7
			HOMO-3 $\rightarrow$ LUMO (d, p ^s $\rightarrow$ D)	38.3
			HOMO-3 $\rightarrow$ LUMO+1 (d, p ^s $\rightarrow$ D)	27.4
			HOMO-4 $\rightarrow$ LUMO (d, p ^s $\rightarrow$ D)	21.8
			HOMO-4 $\rightarrow$ LUMO+1 (d, p ^s $\rightarrow$ D)	10.9

Table S2. Excitation energy, oscillator strength, and details of the transitions and their contributions for $[\text{Au}_{25}(\text{SMe})_{18}]^-$ obtained by TDDFT calculations with PBE. The transitions are shown in terms of the orbital number as well as the interpretations if possible from the superatom perspective; p^s is S (3p).

Excited state	Excitation energy / eV	Oscillator strength	Transitions	Contribution / %
S_1	1.28	4.24×10^{-3}	HOMO $\rightarrow$ LUMO (P $\rightarrow$ D)	78.4
			HOMO $\rightarrow$ LUMO+1 (P $\rightarrow$ D)	11.7
S_2	1.30	1.49×10^{-3}	HOMO-2 $\rightarrow$ LUMO (P $\rightarrow$ D)	66.3
			HOMO $\rightarrow$ LUMO+1 (P $\rightarrow$ D)	10.7
			HOMO-1 $\rightarrow$ LUMO (P $\rightarrow$ D)	9.7
			HOMO-2 $\rightarrow$ LUMO+1 (P $\rightarrow$ D)	5.7
			HOMO-1 $\rightarrow$ LUMO+1 (P $\rightarrow$ D)	89.6
S_3	1.32	1.67×10^{-3}	HOMO-2 $\rightarrow$ LUMO+1 (P $\rightarrow$ D)	6.9
			HOMO $\rightarrow$ LUMO+1 (P $\rightarrow$ D)	66.8
S_4	1.37	3.25×10^{-2}	HOMO-2 $\rightarrow$ LUMO (P $\rightarrow$ D)	17.1
			HOMO $\rightarrow$ LUMO (P $\rightarrow$ D)	9.0
			HOMO-1 $\rightarrow$ LUMO (P $\rightarrow$ D)	84.0
S_5	1.38	2.89×10^{-2}	HOMO $\rightarrow$ LUMO+1 (P $\rightarrow$ D)	7.1
			HOMO-2 $\rightarrow$ LUMO+1 (P $\rightarrow$ D)	79.7
S_6	1.40	2.99×10^{-2}	HOMO $\rightarrow$ LUMO (P $\rightarrow$ D)	6.6
			HOMO-2 $\rightarrow$ LUMO (P $\rightarrow$ D)	5.9
			HOMO-3 $\rightarrow$ LUMO (d, $p^s \rightarrow$ D)	45.2
S_7	2.02	5.64×10^{-10}	HOMO-3 $\rightarrow$ LUMO+1 (d, $p^s \rightarrow$ D)	21.9
			HOMO-4 $\rightarrow$ LUMO (d, $p^s \rightarrow$ D)	18.7
			HOMO-4 $\rightarrow$ LUMO+1 (d, $p^s \rightarrow$ D)	13.9
			HOMO $\rightarrow$ LUMO+2 (P $\rightarrow$ D)	85.6
S_8	2.07	2.40×10^{-4}	HOMO-2 $\rightarrow$ LUMO+2 (P $\rightarrow$ D)	3.9
			HOMO-6 $\rightarrow$ LUMO (d, $p^s \rightarrow$ D)	2.1
			HOMO-3 $\rightarrow$ LUMO (d, $p^s \rightarrow$ D)	48.6
S_9	2.08	4.28×10^{-9}	HOMO-3 $\rightarrow$ LUMO+1 (d, $p^s \rightarrow$ D)	27.7
			HOMO-4 $\rightarrow$ LUMO (d, $p^s \rightarrow$ D)	20.7
			HOMO-4 $\rightarrow$ LUMO (d, $p^s \rightarrow$ D)	51.3
S_{10}	2.09	5.29×10^{-9}	HOMO-3 $\rightarrow$ LUMO+1 (d, $p^s \rightarrow$ D)	45.4
			HOMO $\rightarrow$ LUMO+3 (P $\rightarrow$ D)	31.4
S_{11}	2.10	1.15×10^{-3}	HOMO-5 $\rightarrow$ LUMO (d, $p^s \rightarrow$ D)	29.0
			HOMO-2 $\rightarrow$ LUMO+3 (P $\rightarrow$ D)	10.5
			HOMO-1 $\rightarrow$ LUMO+2 (P $\rightarrow$ D)	10.3
			HOMO-1 $\rightarrow$ LUMO+3 (P $\rightarrow$ D)	8.2

S ₁₂	2.10	3.18×10^{-4}	HOMO-2 $\rightarrow$ LUMO+2 (P $\rightarrow$ D)	4.2
			HOMO-5 $\rightarrow$ LUMO (d, p ^s $\rightarrow$ D)	54.7
			HOMO-2 $\rightarrow$ LUMO+3 (P $\rightarrow$ D)	14.2
			HOMO-1 $\rightarrow$ LUMO+2 (P $\rightarrow$ D)	10.4
			HOMO-2 $\rightarrow$ LUMO+2 (P $\rightarrow$ D)	5.8
S ₁₃	2.11	1.79×10^{-4}	HOMO $\rightarrow$ LUMO+3 (P $\rightarrow$ D)	5.2
			HOMO-1 $\rightarrow$ LUMO+3 (P $\rightarrow$ D)	36.4
			HOMO-2 $\rightarrow$ LUMO+2 (P $\rightarrow$ D)	18.1
			HOMO $\rightarrow$ LUMO+4 (P $\rightarrow$ D)	11.1
			HOMO-5 $\rightarrow$ LUMO+1 (d, p ^s $\rightarrow$ D)	9.7
			HOMO-2 $\rightarrow$ LUMO+3 (P $\rightarrow$ D)	9.0
			HOMO $\rightarrow$ LUMO+3 (P $\rightarrow$ D)	5.6
S ₁₄	2.11	2.73×10^{-9}	HOMO-1 $\rightarrow$ LUMO+2 (P $\rightarrow$ D)	4.3
			HOMO-4 $\rightarrow$ LUMO+1 (d, p ^s $\rightarrow$ D)	82.9
			HOMO-4 $\rightarrow$ LUMO (d, p ^s $\rightarrow$ D)	7.4

Table S3. Excitation energy, oscillator strength, and details of the transitions and their contributions for [Au₂₅(SEtPh)₁₈][−] obtained by TDDFT calculations with PBE. The transitions are shown in terms of the orbital number as well as the interpretations if possible from the superatom perspective; p^s is S (3p).

Excited state	Excitation energy / eV	Oscillator strength	Transitions	Contribution / %
S ₁	1.26	7.89×10^{-3}	HOMO $\rightarrow$ LUMO (P $\rightarrow$ D)	92.4
S ₂	1.33	1.45×10^{-3}	HOMO-2 $\rightarrow$ LUMO (P $\rightarrow$ D)	66.8
			HOMO $\rightarrow$ LUMO+1 (P $\rightarrow$ D)	11.9
			HOMO-2 $\rightarrow$ LUMO+1 (P $\rightarrow$ D)	11.8
			HOMO-1 $\rightarrow$ LUMO+1 (P $\rightarrow$ D)	46.4
S ₃	1.35	1.21×10^{-2}	HOMO-1 $\rightarrow$ LUMO (P $\rightarrow$ D)	22.6
			HOMO $\rightarrow$ LUMO+1 (P $\rightarrow$ D)	16.7
			HOMO-2 $\rightarrow$ LUMO (P $\rightarrow$ D)	13.2
			HOMO-1 $\rightarrow$ LUMO (P $\rightarrow$ D)	63.5
			HOMO $\rightarrow$ LUMO+1 (P $\rightarrow$ D)	17.0
S ₄	1.38	2.56×10^{-2}	HOMO-1 $\rightarrow$ LUMO+1 (P $\rightarrow$ D)	10.9
			HOMO $\rightarrow$ LUMO+1 (P $\rightarrow$ D)	48.0
			HOMO-1 $\rightarrow$ LUMO+1 (P $\rightarrow$ D)	39.7
S ₅	1.40	3.21×10^{-2}	HOMO-2 $\rightarrow$ LUMO (P $\rightarrow$ D)	6.7
			HOMO-2 $\rightarrow$ LUMO+1 (P $\rightarrow$ D)	82.2
S ₆	1.44	3.56×10^{-2}	HOMO-2 $\rightarrow$ LUMO (P $\rightarrow$ D)	10.7

S ₇	1.99	1.04×10^{-6}	HOMO-3 $\rightarrow$ LUMO (d, p ^s $\rightarrow$ D)	91.9
S ₈	2.04	1.25×10^{-3}	HOMO $\rightarrow$ LUMO+4 (P $\rightarrow$ D)	38.8
			HOMO $\rightarrow$ LUMO+2 (P $\rightarrow$ D)	28.2
			HOMO $\rightarrow$ LUMO+3 (P $\rightarrow$ D)	17.6
			HOMO-1 $\rightarrow$ LUMO+4 (P $\rightarrow$ D)	4.6
			HOMO-1 $\rightarrow$ LUMO+2 (P $\rightarrow$ D)	4.2
S ₉	2.06	3.04×10^{-3}	HOMO $\rightarrow$ LUMO+4 (P $\rightarrow$ D)	24.5
			HOMO-1 $\rightarrow$ LUMO+4 (P $\rightarrow$ D)	23.7
			HOMO-1 $\rightarrow$ LUMO+2 (P $\rightarrow$ D)	22.6
			HOMO $\rightarrow$ LUMO+2 (P $\rightarrow$ D)	11.9
			HOMO $\rightarrow$ LUMO+3 (P $\rightarrow$ D)	9.4
S ₁₀	2.06	3.20×10^{-3}	HOMO $\rightarrow$ LUMO+3 (P $\rightarrow$ D)	46.2
			HOMO $\rightarrow$ LUMO+2 (P $\rightarrow$ D)	25.3
			HOMO-2 $\rightarrow$ LUMO+2 (P $\rightarrow$ D)	14.2
			HOMO-5 $\rightarrow$ LUMO (d, p ^s $\rightarrow$ D)	3.6
			HOMO-2 $\rightarrow$ LUMO+3 (P $\rightarrow$ D)	2.8
S ₁₁	2.08	1.47×10^{-4}	HOMO-4 $\rightarrow$ LUMO (d, p ^s $\rightarrow$ D)	73.8
			HOMO-1 $\rightarrow$ LUMO+2 (P $\rightarrow$ D)	5.0
			HOMO-6 $\rightarrow$ LUMO (d, p ^s $\rightarrow$ D)	3.8
			HOMO-1 $\rightarrow$ LUMO+3 (P $\rightarrow$ D)	3.3
			HOMO $\rightarrow$ LUMO+4 (P $\rightarrow$ D)	2.7
S ₁₂	2.08	5.37×10^{-4}	HOMO-2 $\rightarrow$ LUMO+3 (P $\rightarrow$ D)	2.5
			HOMO-4 $\rightarrow$ LUMO (d, p ^s $\rightarrow$ D)	18.6
			HOMO-1 $\rightarrow$ LUMO+2 (P $\rightarrow$ D)	18.3
			HOMO-6 $\rightarrow$ LUMO (d, p ^s $\rightarrow$ D)	13.9
			HOMO-2 $\rightarrow$ LUMO+3 (P $\rightarrow$ D)	12.1
S ₁₃	2.09	4.74×10^{-5}	HOMO-1 $\rightarrow$ LUMO+3 (P $\rightarrow$ D)	11.7
			HOMO $\rightarrow$ LUMO+4 (P $\rightarrow$ D)	10.3
			HOMO-2 $\rightarrow$ LUMO+2 (P $\rightarrow$ D)	5.7
			HOMO-5 $\rightarrow$ LUMO (d, p ^s $\rightarrow$ D)	39.8
			HOMO-2 $\rightarrow$ LUMO+3 (P $\rightarrow$ D)	19.8
S ₁₄	2.10	3.34×10^{-3}	HOMO-6 $\rightarrow$ LUMO (d, p ^s $\rightarrow$ D)	12.9
			HOMO-1 $\rightarrow$ LUMO+2 (P $\rightarrow$ D)	9.7
			HOMO-2 $\rightarrow$ LUMO+2 (P $\rightarrow$ D)	7.5
			HOMO $\rightarrow$ LUMO+4 (P $\rightarrow$ D)	3.8
			HOMO-5 $\rightarrow$ LUMO (d, p ^s $\rightarrow$ D)	23.4
			HOMO-1 $\rightarrow$ LUMO+3 (P $\rightarrow$ D)	20.1
			HOMO-2 $\rightarrow$ LUMO+3 (P $\rightarrow$ D)	17.2

			HOMO-2 $\rightarrow$ LUMO+2 (P $\rightarrow$ D)	13.3
			HOMO-3 $\rightarrow$ LUMO+1 (d, p ^s $\rightarrow$ D)	9.5
			HOMO $\rightarrow$ LUMO+3 (P $\rightarrow$ D)	3.7
			HOMO-1 $\rightarrow$ LUMO+4 (P $\rightarrow$ D)	2.4
			HOMO-7 $\rightarrow$ LUMO (d, p ^s $\rightarrow$ D)	2.4

Table S4. Transition dipole moments from ideal P orbitals to D orbitals.

Initial orbitals	Coordinates	Final orbitals	$\mu^2/(\int r^6 f_1(r)f_2(r) dr)^2$	Ratio
P _x	x	D _{x2-y2}	$(4\pi/15)^2$	1
	y		0	
	z		0	
P _x	x	D _{z2}	$(4\pi\sqrt{3}/15)^2$	3
	y		0	
	z		0	
P _y	x	D _{x2-y2}	0	1
	y		$(4\pi/15)^2$	
	z		0	
P _y	x	D _{z2}	0	3
	y		$(4\pi\sqrt{3}/15)^2$	
	z		0	
P _z	x	D _{x2-y2}	0	
	y		0	
	z		0	
P _z	x	D _{z2}	0	12
	y		0	
	z		$(8\pi\sqrt{3}/15)^2$	

Table S5. The emission energy, oscillator strength, and major transition at **S**_{1MIN} obtained by geometry optimizations starting from various initial structures for [Au₂₅(SMe)₁₈][−] with B3LYP.

Initial structure	Emission energy / eV	Oscillator strength	Major transition	Contribution / %
S _{0MIN}	0.91	1.06×10^{-2}	HOMO $\rightarrow$ LUMO (P $\rightarrow$ D)	98.3
S _{7MIN} ^{em}	0.88	9.70×10^{-3}	HOMO $\rightarrow$ LUMO (P $\rightarrow$ D)	98.6
S _{7MIN} ^{non}	0.88	8.50×10^{-3}	HOMO $\rightarrow$ LUMO (P $\rightarrow$ D)	99.0

Table S6. The emission energies after geometry optimization in the respective $S_2 \sim S_6$ states from various initial structures for $[\text{Au}_{25}(\text{SMe})_{18}]^-$ with B3LYP.

Initial structure	Optimized state	Emission energy / eV	Energy gap with the next lower state / eV
$S_{0\text{MIN}}$	S_2 (not converged)	1.16	0.01
	S_3 (not converged)	1.26	0.00
	S_4	1.33	0.00
	S_5	1.44	0.00
	S_6 (not converged)	1.46	0.00
$S_{7\text{MIN}}^{\text{em}}$	S_2 (not converged)	1.11	0.00
	S_3 (not converged)	1.29	0.00
	S_4	1.32	0.00
	S_5 (not converged)	1.43	0.00
	S_6 (not converged)	1.46	0.00
$S_{7\text{MIN}}^{\text{non}}$	S_2 (not converged)	1.10	0.00
	S_3 (not converged)	1.25	0.00
	S_4 (not converged)	1.35	0.00
	S_5 (not converged)	1.43	0.00
	S_6 (not converged)	1.46	0.00

Table S7. Averaged values and standard deviations of Au^c-Au^s and Au^s-S bond distances after geometry optimization for [Au₂₅(SMe)₁₈]⁻, [Au₂₅(SEtPh)₁₈]⁻ and [Au₂₅(SH)₁₈]⁻ in the S₀ state with C₁ or C_i symmetry by DFT computations using PBE or B3LYP functionals. See Table 2 for the abbreviations.

Species	Symmetry	Functional	Au ^c -Au ^s / Å	Au ^s -S / Å
[Au ₂₅ (SMe) ₁₈] ⁻	C ₁	PBE	2.870 ± 0.008	2.481 ± 0.004
	C ₁	B3LYP	2.903 ± 0.010	2.518 ± 0.003
[Au ₂₅ (SEtPh) ₁₈] ⁻	C ₁	PBE	2.870 ± 0.013	2.483 ± 0.007
[Au ₂₅ (SH) ₁₈] ⁻	C ₁	PBE	2.864 ± 0.004	2.498 ± 0.007
	C _i		2.864 ± 0.004	2.497 ± 0.004

References

- (1) Wang, G.; Huang, T.; Murray, R. W.; Menard, L.; Nuzzo, R. G. Near-IR Luminescence of Monolayer-Protected Metal Clusters. *J. Am. Chem. Soc.* **2005**, *127*, 812–813.
- (2) Kawasaki, H.; Hamaguchi, K.; Osaka, I.; Arakawa, R. pH-Dependent Synthesis of Pepsin-Mediated Gold Nanoclusters with Blue Green and Red Fluorescent Emission. *Adv. Funct. Mater.* **2011**, *21*, 3508–3515.
- (3) Maity, P.; Takano, S.; Yamazoe, S.; Wakabayashi, T.; Tsukuda, T. Binding Motif of Terminal Alkynes on Gold Clusters. *J. Am. Chem. Soc.* **2013**, *135*, 9450–9457.
- (4) Stampelcoskie, K. G.; Chen, Y.; Kamat, P. V. Excited-State Behavior of Luminescent Glutathione-Protected Gold Clusters. *J. Phys. Chem. C* **2014**, *118*, 1370–1376.
- (5) Mohanty, J. S.; Baksi, A.; Haiwon, L.; Pradeep, T. Noble Metal Clusters Protected with Mixed Proteins Exhibit Intense Photoluminescence. *RSC Adv.* **2015**, *5*, 48039–48045.
- (6) Pyo, K.; Thanthirige, V. D.; Kwak, K.; Pandurangan, P.; Ramakrishna, G.; Lee, D. Ultrabright Luminescence from Gold Nanoclusters: Rigidifying the Au(I)-Thiolate Shell. *J. Am. Chem. Soc.* **2015**, *137*, 8244–8250.
- (7) Chen, P.; Periasamy, A. P.; Harroun, S. G.; Wu, W.; Chang, H. Photoluminescence Sensing Systems Based on Copper, Gold and Silver Nanomaterials. *Coord. Chem. Rev.* **2016**, *320–321*, 129–138.
- (8) Goswami, N.; Yao, Q.; Luo, Z.; Li, J.; Chen, T.; Xie, J. Luminescent Metal Nanoclusters with Aggregation-

Induced Emission. *J. Phys. Chem. Lett.* **2016**, *7*, 962–975.

- (9) Song, X.-R.; Goswami, N.; Yang, H.-H.; Xie, J. Functionalization of Metal Nanoclusters for Biomedical Applications. *Analyst* **2016**, *141*, 3126–3140.
- (10) Gan, Z.; Chen, J.; Wang, J.; Wang, C.; Li, M.; Yao, C.; Zhuang, S.; Xu, A.; Li, L.; Wu, Z. The Fourth Crystallographic Closest Packing Unveiled in the Gold Nanocluster Crystal. *Nat. Commun.* **2017**, *8*, 14739–14744.
- (11) Häkkinen, H. Atomic and Electronic Structure of Gold Clusters: Understanding Flakes, Cages and Superatoms from Simple Concepts. *Chem. Soc. Rev.* **2008**, *37*, 1847–1859.
- (12) Walter, M.; Akola, J.; Lopez-Acevedo, O.; Jadzinsky, P. D.; Calero, G.; Ackerson, C. J.; Whetten, R. L.; Grönbeck, H.; Häkkinen, H. A Unified View of Ligand-Protected Gold Clusters as Superatom Complexes. *Proc. Natl. Acad. Sci.* **2008**, *105*, 9157–9162.
- (13) Jin, R. Quantum Sized, Thiolate-Protected Gold Nanoclusters. *Nanoscale* **2010**, *2*, 343–362.
- (14) Akola, J.; Kacprzak, K. A.; Lopez-Acevedo, O.; Walter, M.; Grönbeck, H.; Häkkinen, H. Thiolate-Protected Au₂₅ Superatoms as Building Blocks: Dimers and Crystals. *J. Phys. Chem. C* **2010**, *114*, 15986–15994.
- (15) Tofanelli, M. A.; Ackerson, C. J. Superatom Electron Configuration Predicts Thermal Stability of Au₂₅(SR)₁₈ Nanoclusters. *J. Am. Chem. Soc.* **2012**, *134*, 16937–16940.
- (16) Jiang, D. The Expanding Universe of Thiolated Gold Nanoclusters and Beyond. *Nanoscale* **2013**, *5*, 7149–7160.
- (17) Ma, Z.; Wang, P.; Xiong, L.; Pei, Y. Thiolate-Protected Gold Nanoclusters: Structural Prediction and the Understandings of Electronic Stability from First Principles Simulations. *Wiley Interdiscip. Rev. Comput. Mol. Sci.* **2017**, *7*, 1–19.
- (18) Yanagimoto, Y.; Negishi, Y.; Fujihara, H.; Tsukuda, T. Chiroptical Activity of BINAP-Stabilized Undecagold Clusters. *J. Phys. Chem. B* **2006**, *110*, 11611–11614.
- (19) Dolamic, I.; Knoppe, S.; Dass, A.; Bürgi, T. First Enantioseparation and Circular Dichroism Spectra of Au₃₈ Clusters Protected by Achiral Ligands. *Nat. Commun.* **2012**, *3*, 798–803.
- (20) Knoppe, S.; Dolamic, I.; Dass, A.; Bürgi, T. Separation of Enantiomers and CD Spectra of

- $\text{Au}_{40}(\text{SCH}_2\text{CH}_2\text{Ph})_{24}$: Spectroscopic Evidence for Intrinsic Chirality. *Angew. Chem. Int. Ed.* **2012**, *51*, 7589–7591.
- (21) Zhu, Y.; Qian, H.; Jin, R. Catalysis Opportunities of Atomically Precise Gold Nanoclusters. *J. Mater. Chem.* **2011**, *21*, 6793–6799.
- (22) Pei, Y.; Zeng, X. C. Investigating the Structural Evolution of Thiolate Protected Gold Clusters from First-Principles. *Nanoscale* **2012**, *4*, 4054–4072.
- (23) Li, G.; Jin, R. Atomically Precise Gold Nanoclusters as New Model Catalysts. *Acc. Chem. Res.* **2013**, *46*, 1749–1758.
- (24) Yamazoe, S.; Koyasu, K.; Tsukuda, T. Nonscalable Oxidation Catalysis of Gold Clusters. *Acc. Chem. Res.* **2014**, *47*, 816–824.
- (25) Zhu, M.; Aikens, C. M.; Hendrich, M. P.; Gupta, R.; Qian, H.; Schatz, G. C.; Jin, R. Reversible Switching of Magnetism in Thiolate-Protected Au_{25} Superatoms. *J. Am. Chem. Soc.* **2009**, *131*, 2490–2492.
- (26) Reveles, J. U.; Clayborne, P. A.; Reber, A. C.; Khanna, S. N.; Pradhan, K.; Sen, P.; Pederson, M. R. Designer Magnetic Superatoms. *Nat. Chem.* **2009**, *1*, 310–315.
- (27) Nealon, G. L.; Donnio, B.; Greget, R.; Kappler, J.-P.; Terazzi, E.; Gallani, J.-L. Magnetism in Gold Nanoparticles. *Nanoscale* **2012**, *4*, 5244–5258.
- (28) Heaven, M. W.; Dass, A.; White, P. S.; Holt, K. M.; Murray, R. W. Crystal Structure of the Gold Nanoparticle $[\text{N}(\text{C}_8\text{H}_{17})_4][\text{Au}_{25}(\text{SCH}_2\text{CH}_2\text{Ph})_{18}]$. *J. Am. Chem. Soc.* **2008**, *130*, 3754–3755.
- (29) Akola, J.; Walter, M.; Whetten, R. L.; Häkkinen, H.; Grönbeck, H. On the Structure of Thiolate-Protected Au_{25} . *J. Am. Chem. Soc.* **2008**, *130*, 3756–3757.
- (30) Zhu, M.; Aikens, C. M.; Hollander, F. J.; Schatz, G. C.; Jin, R. Correlating the Crystal Structure of A Thiol-Protected Au_{25} Cluster and Optical Properties. *J. Am. Chem. Soc.* **2008**, *130*, 5883–5885.
- (31) Aikens, C. M. Origin of Discrete Optical Absorption Spectra of $\text{M}_{25}(\text{SH})_{18}^-$ Nanoparticles ($\text{M} = \text{Au}, \text{Ag}$). *J. Phys. Chem. C* **2008**, *112*, 19797–19800.
- (32) Aikens, C. M. Electronic Structure of Ligand-Passivated Gold and Silver Nanoclusters. *J. Phys. Chem. Lett.* **2011**, *2*, 99–104.

- (33) Bigioni, T. P.; Whetten, R. L.; Dag, Ö. Near-Infrared Luminescence from Small Gold Nanocrystals. *J. Phys. Chem. B* **2000**, *104*, 6983–6986.
- (34) Huang, T.; Murray, R. W. Visible Luminescence of Water-Soluble Monolayer-Protected Gold Clusters. *J. Phys. Chem. B* **2001**, *105*, 12498–12502.
- (35) Lee, D.; Donkers, R. L.; Wang, G.; Harper, A. S.; Murray, R. W. Electrochemistry and Optical Absorbance and Luminescence of Molecule-like Au₃₈ Nanoparticles. *J. Am. Chem. Soc.* **2004**, *126*, 6193–6199.
- (36) Wang, G.; Guo, R.; Kalyuzhny, G.; Choi, J.-P.; Murray, R. W. NIR Luminescence Intensities Increase Linearly with Proportion of Polar Thiolate Ligands in Protecting Monolayers of Au₃₈ and Au₁₄₀ Quantum Dots. *J. Phys. Chem. B* **2006**, *110*, 20282–20289.
- (37) Aikens, C. M. Geometric and Electronic Structure of Au₂₅(SPhX)₁₈[−] (X = H, F, Cl, Br, CH₃, and OCH₃). *J. Phys. Chem. Lett.* **2010**, *1*, 2594–2599.
- (38) Parker, J. F.; Fields-Zinna, C. A.; Murray, R. W. The Story of a Monodisperse Gold Nanoparticle: Au₂₅L₁₈. *Acc. Chem. Res.* **2010**, *43*, 1289–1296.
- (39) Green, T. D.; Yi, C.; Zeng, C.; Jin, R.; McGill, S.; Knappenberger, K. L. J. Temperature-Dependent Photoluminescence of Structurally-Precise Quantum-Confined Au₂₅(SC₈H₉)₁₈ and Au₃₈(SC₁₂H₂₅)₂₄ Metal Nanoparticles. *J. Phys. Chem. A* **2014**, *118*, 10611–10621.
- (40) Jiang, D.; Kühn, M.; Tang, Q.; Weigend, F. Superatomic Orbitals under Spin-Orbit Coupling. *J. Phys. Chem. Lett.* **2014**, *5*, 3286–3289.
- (41) Kawasaki, H.; Kumar, S.; Li, G.; Zeng, C.; Kauffman, D. R.; Yoshimoto, J.; Iwasaki, Y.; Jin, R. Generation of Singlet Oxygen by Photoexcited Au₂₅(SR)₁₈ Clusters. *Chem. Mater.* **2014**, *26*, 2777–2788.
- (42) Yu, P.; Wen, X.; Toh, Y.-R.; Ma, X.; Tang, J. Fluorescent Metallic Nanoclusters: Electron Dynamics, Structure, and Applications. *Part. Part. Syst. Charact.* **2015**, *32*, 142–163.
- (43) Yuan, X.; Goswami, N.; Chen, W.; Yao, Q.; Xie, J. Insights into the Effect of Surface Ligands on the Optical Properties of Thiolated Au₂₅ Nanoclusters. *Chem. Commun.* **2016**, *52*, 5234–5237.
- (44) Tofanelli, M. A.; Salorinne, K.; Ni, T. W.; Malola, S.; Newell, B.; Phillips, B.; Häkkinen, H.; Ackerson, C. J. Jahn–Teller Effects in Au₂₅(SR)₁₈. *Chem. Sci.* **2016**, *7*, 1882–1890.

- (45) Negishi, Y.; Kurashige, W.; Niihori, Y.; Nobusada, K. Toward the Creation of Stable, Functionalized Metal Clusters. *Phys. Chem. Chem. Phys.* **2013**, *15*, 18736–18751.
- (46) Jin, R.; Nobusada, K. Doping and Alloying in Atomically Precise Gold Nanoparticles. *Nano Res.* **2014**, *7*, 285–300.
- (47) Barcaro, G.; Sementa, L.; Fortunelli, A.; Stener, M. Optical Properties of Nanoalloys. *Phys. Chem. Chem. Phys.* **2015**, *17*, 27952–27967.
- (48) Zhong, J.; Tang, X.; Tang, J.; Su, J.; Pei, Y. Density Functional Theory Studies on Structure, Ligand Exchange, and Optical Properties of Ligand-Protected Gold Nanoclusters: Thiolate versus Selenolate. *J. Phys. Chem. C* **2015**, *119*, 9205–9214.
- (49) Pohjolainen, E.; Häkkinen, H.; Clayborne, A. The Role of the Anchor Atom in the Ligand of the Monolayer-Protected Au₂₅(SR)₁₈[−] Nanocluster. *J. Phys. Chem. C* **2015**, *119*, 9587–9594.
- (50) Zhou, M.; Qian, H.; Sfeir, M. Y.; Nobusada, K.; Jin, R. Effects of Single Atom Doping on the Ultrafast Electron Dynamics of M₁Au₂₄(SR)₁₈ (M = Pd, Pt) Nanoclusters. *Nanoscale* **2016**, *8*, 7163–7171.
- (51) Wu, Z.; Jin, R. On the Ligand's Role in the Fluorescence of Gold Nanoclusters. *Nano Lett.* **2010**, *10*, 2568–2573.
- (52) Weerawardene, K. L. D. M.; Aikens, C. M. Theoretical Insights into the Origin of Photoluminescence of Au₂₅(SR)₁₈[−] Nanoparticles. *J. Am. Chem. Soc.* **2016**, *138*, 11202–11210.
- (53) Link, S.; Beeby, A.; Fitzgerald, S.; El-sayed, M. A.; Schaaff, T. G.; Whetten, R. L. Visible to Infrared Luminescence from a 28-Atom Gold Cluster. *J. Phys. Chem. B* **2002**, *106*, 3410–3415.
- (54) Ramakrishna, G.; Varnavski, O.; Kim, J.; Lee, D.; Goodson, T. Quantum-Sized Gold Clusters as Efficient Two-Photon Absorbers. *J. Am. Chem. Soc.* **2008**, *130*, 5032–5033.
- (55) Varnavski, O.; Ramakrishna, G.; Kim, J.; Lee, D.; Goodson, T. Critical Size for the Observation of Quantum Confinement in Optically Excited Gold Clusters. *J. Am. Chem. Soc.* **2010**, *132*, 16–17.
- (56) Devadas, M. S.; Kim, J.; Sinn, E.; Lee, D.; III, Goodson, T.; Ramakrishna, G. Unique Ultrafast Visible Luminescence in Monolayer-Protected Au₂₅ Clusters. *J. Phys. Chem. C* **2010**, *114*, 22417–22423.
- (57) Yau, S. H.; Varnavski, O.; Gilbertson, J. D.; Chandler, B.; Ramakrishna, G.; III, Goodson, T. Ultrafast

- Optical Study of Small Gold Monolayer Protected Clusters: A Closer Look at Emission. *J. Phys. Chem. C* **2010**, *114*, 15979–15985.
- (58) Yau, S. H.; Varnavski, O.; III, Goodson, T. An Ultrafast Look at Au Nanoclusters. *Acc. Chem. Res.* **2013**, *46*, 1506–1516.
- (59) Miller, S. A.; Womick, J. M.; Parker, J. F.; Murray, R. W.; Moran, A. M. Femtosecond Relaxation Dynamics of Au₂₅L₁₈[−] Monolayer-Protected Clusters. *J. Phys. Chem. C* **2009**, *113*, 9440–9444.
- (60) Stoll, T.; Sgrò, E.; Jarrett, J. W.; Réhault, J.; Oriana, A.; Sala, L.; Branchi, F.; Cerullo, G.; Knappenberger, K. L. J. Superatom State-Resolved Dynamics of the Au₂₅(SC₈H₉)₁₈[−] Cluster from Two-Dimensional Electronic Spectroscopy. *J. Am. Chem. Soc.* **2016**, *138*, 1788–1791.
- (61) Yi, C.; Zheng, H.; Herbert, P. J.; Chen, Y.; Jin, R.; Knappenberger, K. L. J. Ligand- and Solvent-Dependent Electronic Relaxation Dynamics of Au₂₅(SR)₁₈[−] Monolayer-Protected Clusters. *J. Phys. Chem. C* **2017**, *121*, 24894–24902.
- (62) Senanayake, R. D.; Akimov, A. V.; Aikens, C. M. Theoretical Investigation of Electron and Nuclear Dynamics in the [Au₂₅(SH)₁₈][−] Thiolate-Protected Gold Nanocluster. *J. Phys. Chem. C* **2017**, *121*, 10653–10662.
- (63) Chen, X.; Prezhdov, O. V.; Ma, Z.; Hou, T.; Guo, Z.; Li, Y. Ab Initio Phonon-Coupled Nonadiabatic Relaxation Dynamics of [Au₂₅(SH)₁₈][−] Clusters. *Phys. Status Solidi B* **2016**, *253*, 458–462.
- (64) TURBOMOLE V7.0.1-7.1, A Development of University of Karlsruhe and Forschungszentrum Karlsruhe GmbH, 1989-2007, TURBOMOLE GmbH, since 2007; Available from <http://www.turbomole.com>.
- (65) Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* **1996**, *77*, 3865–3868.
- (66) Becke, A. D. Density-Functional Exchange-Energy Approximation with Correct Asymptotic Behavior. *Phys. Rev. A* **1988**, *38*, 3098–3100.
- (67) Lee, C.; Yang, W.; Parr, R. G. Development of the Colle-Salvetti Correlation-Energy Formula into a Functional of the Electron Density. *Phys. Rev. B* **1988**, *37*, 785–789.
- (68) Becke, A. D. Density-Functional thermochemistry.III. The Role of Exact Exchange. *J. Chem. Phys.* **1993**,

98, 5648–5652.

- (69) Andrae, D.; Häußermann, U.; Dolg, M.; Stoll, H.; Preuß, H. T. Energy-Adjusted Ab Initio Pseudopotentials for the Second and Third Row Transition Elements. *Theor. Chim. Acta* **1990**, *77*, 123–141.
- (70) Yanai, T.; Tew, D. P.; Handy, N. C. A New Hybrid Exchange – Correlation Functional Using the Coulomb-Attenuating Method (CAM-B3LYP). *Chem. Phys. Lett.* **2004**, *393*, 51–57.
- (71) Weigend, F.; Ahlrichs, R. Balanced Basis Sets of Split Valence, Triple Zeta Valence and Quadruple Zeta Valence Quality for H to Rn: Design and Assessment of Accuracy. *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297–3305.
- (72) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Petersson, G. A.; Nakatsuji, H.; et al. Gaussian09. Gaussian Inc.: Wallingford, CT 2009.
- (73) Momma, K.; Izumi, F. VESTA: A Three-Dimensional Visualization System for Electronic and Structural Analysis. *J. Appl. Crystallogr.* **2008**, *41*, 653–658.
- (74) Zhu, M.; Eckenhoff, W. T.; Pintauer, T.; Jin, R. Conversion of Anionic $[\text{Au}_{25}(\text{SCH}_2\text{CH}_2\text{Ph})_{18}]^-$ Cluster to Charge Neutral Cluster via Air Oxidation. *J. Phys. Chem. C* **2008**, *112*, 14221–14224.
- (75) Tlahuice-Flores, A.; Whetten, R. L.; Jose-Yacamán, M. Ligand Effects on the Structure and the Electronic Optical Properties of Anionic $\text{Au}_{25}(\text{SR})_{18}$ Clusters. *J. Phys. Chem. C* **2013**, *117*, 20867–20875.
- (76) Bakar, M. A.; Sugiuchi, M.; Iwasaki, M.; Shichibu, Y.; Konishi, K. Hydrogen Bonds to Au Atoms in Coordinated Gold Clusters. *Nat. Commun.* **2017**, *8*, 576–582.
- (77) Atkins Peter, Overton Tina, Rourke Jon, Weeler Mark, A. F. *SHRIVER&ATKINS Inorganic Chemistry*, 4th ed.; Oxford, 2006.
- (78) Kasha, M. Characterization of Electronic Transitions in Complex Molecules. *Discuss. Faraday Soc.* **1950**, *9*, 14–19.
- (79) Shevyakov, S. V.; Li, H.; Muthyala, R.; Asato, A. E.; Croney, J. C.; Jameson, D. M.; Liu, R. S. H. Orbital Control of the Color and Excited State Properties of Formylated and Fluorinated Derivatives of Azulene. *J. Phys. Chem. A* **2003**, *107*, 3295–3299.
- (80) Johansson, M. P.; Sundholm, D.; Vaara, J. Au_{32} : A 24-Carat Golden Fullerene. *Angew. Chem. Int. Ed.* **2004**,

43, 2678–2681.

- (81) Wang, S. G.; Schwarz, W. H. E. Quasi-Relativistic Density Functional Study of Auophilic Interactions. *J. Am. Chem. Soc.* **2004**, *126*, 1266–1276.
- (82) Pyykkö, P. Theoretical Chemistry of Gold. *Angew. Chem. Int. Ed.* **2004**, *43*, 4412–4456.
- (83) Mendizabal, F.; Aguilera, B.; Olea-Azar, C. Theoretical Study on Electronic Spectra and Auophilic Attraction in $[\text{Au}_3(\text{MeN}=\text{COMe})_3]_n$ ($n=1-4$) Complexes. *Chem. Phys. Lett.* **2007**, *447*, 345–351.
- (84) Pyykkö, P. Theoretical Chemistry of Gold. III. *Chem. Soc. Rev.* **2008**, *37*, 1967–1997.
- (85) Takagi, N.; Ishimura, K.; Matsui, M.; Fukuda, R.; Matsui, T.; Nakajima, T.; Ehara, M.; Sakaki, S. How Can We Understand Au_8 Cores and Entangled Ligands of Selenolate- and Thiolate-Protected Gold Nanoclusters $\text{Au}_{24}(\text{ER})_{20}$ and $\text{Au}_{20}(\text{ER})_{16}$ ($\text{E} = \text{Se}, \text{S}; \text{R} = \text{Ph}, \text{Me}$)? A Theoretical Study. *J. Am. Chem. Soc.* **2015**, *137*, 8593–8602.

Chapter 3: Low-lying Excited States of hqxcH and Zn-hqxc

Complex: Toward Understanding Excited States

Intramolecular Proton Transfer Emission

3.1. Introduction

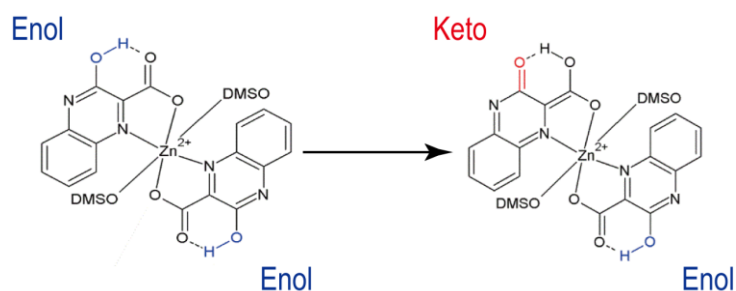
In general, photoluminescence from a molecule originates from the first excited states of either a spin singlet or triplet, according to Kasha's rule. Some molecules, however, show multiple emissions ascribed to various intra- and inter-molecular interactions (e.g. photoinduced electron transfer, fluorescence resonance energy transfer, excimer/exciple) ¹⁻³ and specific excited states which violate Kasha's rule or have several minima in their lowest excited state potential energy surfaces. ^{4,5} Multiple emissions have gained considerable attention for physical chemistry interests, as well as potential applications for in bioimaging, ⁶ sensors, ⁷ and organic electronics materials. ⁸ In addition, photoluminescence associated with an excited state intramolecular proton transfer (ESIPT) has attracted much attention due to its unique photophysical properties, such as multiple emissions due to an isomerization reaction (ex. keto-enol tautomerization) via ESIPT through the intramolecular hydrogen bond. ⁹⁻¹⁴ Many organic molecules showing ESIPT emission are already known, with some showing a high emission quantum yield due to a large Stokes shift ^{15,16} and generating white light based on multiple emissions complementing each other. ¹⁷⁻²² ESIPT can occur in both the solid state ^{23,24} and in solution. For the latter, ESIPT emissions are sensitive to external environment factors such as pH, ^{25,26} solvent polarity, ²⁷⁻²⁹ temperature, ^{30,31} and binding to metal cations and anions. ³²⁻⁴⁰

ESIPT is known to occur on a several hundred femtosecond time scale based on pump-probe measurements, ⁴¹⁻⁴³ even in a rigid glass at low temperature. ⁴⁴ A transient vibrational spectroscopic study revealed a molecular isomerization in the excited state, ⁴⁵ and a large dependence of proton transfer efficiency on solvent polarity. ⁴⁶ A combined experimental and theoretical study on molecular vibrations thoroughly explained the difference between two similar molecules via the structural changes occurring after isomerization. ⁴⁷ Solvent effects on the quantum yield of ESIPT emissions were clarified by theoretical studies on the excited states, where solvents can change activation

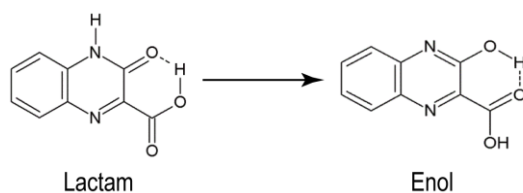
energies in the excited states and the structures in conical intersections.^{48,49} The importance of the intramolecular charge transfer (ICT) state and the aromaticity, which are integral to the ESIPT process, was also pointed out.^{50,51} The $^1\pi\pi^*$ state can enhance the intramolecular hydrogen bonding interaction, thus lowering the energy barrier for the proton transfer as compared to other states (ex. $^1n\pi^*$, $^3\pi\pi^*$ states).^{52,53} In addition to the widely used time-dependent density functional theory (TDDFT) for excited state potential energy surfaces, high-level quantum chemical calculations were performed for mechanistic understanding, as well as substituent and solvent effects.⁵² A recent study combining TDDFT and algebraic diagrammatic construction investigated excited state potential energy surfaces of potential dye molecules for tuning the dual emission behavior in ESIPT.^{53–55}

Because ESIPT organic molecules change their properties based on external environment,^{43–47} introducing metal into ESIPT molecules can enhance their photophysical properties. Heavy metals can lead to phosphorescence in addition to fluorescence by facilitating intersystem crossings.^{56–60} For a large effect from the heavy metals, spin-orbit coupling (SOC) is also required to evaluate the photophysical properties of the metal complexes.^{61,62} Recently, *ab initio* surface hopping molecular dynamics approach has been developed to include both nonadiabatic coupling and spin-orbit coupling effects, and applied to the photodissociation of organic molecule.⁶³ In more advanced way, theoretical approach has been developed to treat spin-vibronic coupling for the intersystem crossing.^{64,65} In sharp contrast to the number of studies on ESIPT organic molecules, the number of studies on metal complexes showing ESIPT is very limited.^{66–71} One reason may be that the ESIPT active sites could possibly be coordinated by a metal atom, thus losing their activity. Careful design for separation of isomerization and coordination sites is required. In this study, we focus on $[\text{Zn}(\text{hqxc})_2(\text{DMSO})_2]$ (Zn-hqxc: hqxc = 3-hydroxy-2-quinoxalinecarboxylate, DMSO = dimethylsulfoxide), which is one successful complex which shows ESIPT emission in the solid state.⁷² The emissions of the Zn-hqxc complex are recorded at 2.35 eV and 2.58–2.92 eV, and from the extent of the Stokes shifts, these emissions are thought to be fluorescence caused by the enol-enol form and the keto-enol form for the two hqcx ligands (see Scheme 1 for the label). These states are derived from keto-enol tautomerization on one of the hqxc ligands (Scheme 1). Interestingly, the hqxcH ligand itself does not show ESIPT emission. The pure hqxcH ligand takes its lactam form (3,4-dihydro-3-oxo-2-quinoxalinecarboxylic acid), while the enol form (3-hydroxy-2-quinoxalinecarboxylic acid) is taken in the Zn-hqxc complex, as shown by single-crystal X-ray diffraction

spectroscopy.⁷² This structural change is important for ESIPT (Scheme 2). In the ground states, structural and vibrational properties for both the lactam and enol forms were investigated,^{73,74} while the properties for their excited states and thus the emission mechanisms for the hqxcH and the Zn-hqxc complex remain undetermined. Thus, in the pursuit of designing new functional materials, experimental and theoretical elucidations of their excited state structural changes and emission mechanisms are mandatory.



Scheme 1. Keto-enol tautomerization via ESIPT. We label the left and right complexes as enol-enol and keto-enol, respectively.



Scheme 2. Lactam form isomerized to enol form

In this paper, we studied the excited states of hqxcH and the Zn-hqxc complex using TDDFT calculations. Our aim is to understand the reason why hqxcH does not show ESIPT, the excited state properties of the Zn-hqxc complex, and the role of the zinc atom. This is the first theoretical study on the excited states of these systems, and we expect that this study builds the basis for designing new ESIPT photonic materials.

3.2. COMPUTATIONAL DETAILS

All structures were optimized in the gas phase by using density functional theory (DFT) and time-dependent DFT (TDDFT) calculations as implemented in Gaussian 09.⁷⁵ The T_1 state was optimized by spin-unrestricted DFT calculations (the spin contamination was verified to be negligible in all cases). Initial structures for the hqxcH and Zn-hqxc complex were taken from their single crystal X-ray diffraction structures. The transition state (TS) geometries and intrinsic reaction coordinate (IRC)⁷⁶ paths were calculated by Gaussian 16.⁷⁷ The M06⁷⁸ exchange-correlation functional with the SDD (Zn)⁷⁹ and cc-pVDZ (other atoms)⁸⁰ basis sets were mainly used. Other exchange-correlation functionals such as B3LYP,^{81–83} CAM-B3LYP,⁸⁴ and BHandHLYP⁸⁵ were also used to check some of the optimized structures for the Zn-hqxc complex. The excited state geometry optimizations varied slightly depending on the functionals, while variation in the Raman spectra was rather minor (Supporting Information). The second-order approximate coupled-cluster (CC2)⁸⁶ calculation with def-SVP⁸⁷ basis sets and the Resolution of Identity approximation was also carried out to check the accuracy of the excitation energies calculated by DFT methods, using Turbomole package 7.3.⁸⁸

To observe the mechanical effects of surrounding molecules, two-layer ONIOM⁸⁹ calculations were carried out, where the DFT and the universal force field⁹⁰ were used for the high and low layers, respectively. The geometries of the high layer were optimized with the surrounding molecules in the low layer fixed. The vibrational analyses for the optimized structures in the ground and excited states have all real-number frequencies (confirming local minima).

To evaluate the possibility of the intersystem crossing between the singlet and triplet states, the spin-orbit coupling term was also calculated for Zn-hqxc complex at the level of the state-averaged complete active space multi-configurational self-consistent field (SA-CASSCF) method⁹¹ with 6-31G** basis sets⁹² using Molpro 2012,⁹³ where the active space contains 14 electrons in 10 orbitals with 134 orbitals from the bottom to be frozen to reduce the computational cost. To reproduce the excited states calculated by the TDDFT method, three singlet and eight triplet states were included in a state-average scheme with equal weights.

All the structures were visualized with Mercury 3.10.1.⁹⁴ For UV-vis absorption and IR/Raman spectra, the line spectra obtained by the TDDFT calculations with harmonic approximation were broadened by a Lorentzian of width

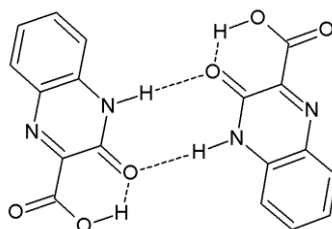
10 nm and 10 cm⁻¹, respectively. Raman spectra were calculated using an excitation wavelength of 1064 nm for the polarizability.⁷³ For discussing intersystem crossing in the hqxcH and obtaining reaction barriers for couples of minima of the Zn-hqxc complex, single point calculations were performed for twelve structures linearly interpolating these double-end structures. The density of states (DOS) spectrum of the Zn-hqxc complex obtained based on the Mulliken population analysis was drawn using GaussSum 3.0 with a full-width at half-maximum of 0.3.⁹⁵

3.3. RESULTS AND DISCUSSION

3.3.1. Computational model: effects of intermolecular interactions

First, we would like to discuss the computational models. As indicated in the single-crystal XRD spectra,⁷² hqxcH can have both intramolecular and intermolecular hydrogen bonds. We believe that ESIPT occurs within the molecule, while the intermolecular hydrogen bond interaction can also affect ESIPT. We compared the IR and Raman spectra of the hqxcH and hqxcH dimer with experimental results. For the Zn-hqxc complex, the intermolecular hydrogen bond interaction seems to be negligible based on the XRD pattern.⁷²

The monomer of hqxcH, as mentioned earlier, can take lactam, enol, and keto forms. We consider the lactam form because it is experimentally observed in the solid, although the enol form was slightly more stable than the lactam form by 0.10 eV in our gas phase geometry optimizations, as shown in previous reports.^{73,74} For a dimer, two hqxcH molecules with an intermolecular hydrogen bond (N-H...O) are considered from the XRD results (Scheme 3). The N-H stretching mode largely shifts to a lower frequency due to the intermolecular hydrogen bonding interaction, approaching the experimental peak position (Supporting Information).⁷³ In contrast, the O-H stretching mode in the monomer is closer to the experimental results than in the dimer, indicating the co-existence of both dimer and



Scheme 3. Lactam form dimer

monomer hqxcH. In fact, there are two crystallographically independent molecules in a unit cell of hqxcH.⁷² We have also performed geometry optimizations for the dimer surrounded by 62 force-field molecules using ONIOM (Figure 1a). The largest bond distance changes are within 0.1 Å, suggesting a minor mechanical effect from surrounding molecules. The vibrational spectra suggest the importance of the dimer model for hqxcH. Particularly, since our aim is to study ESIPT, we will study excited states of both the monomer and the dimer of hqxcH.

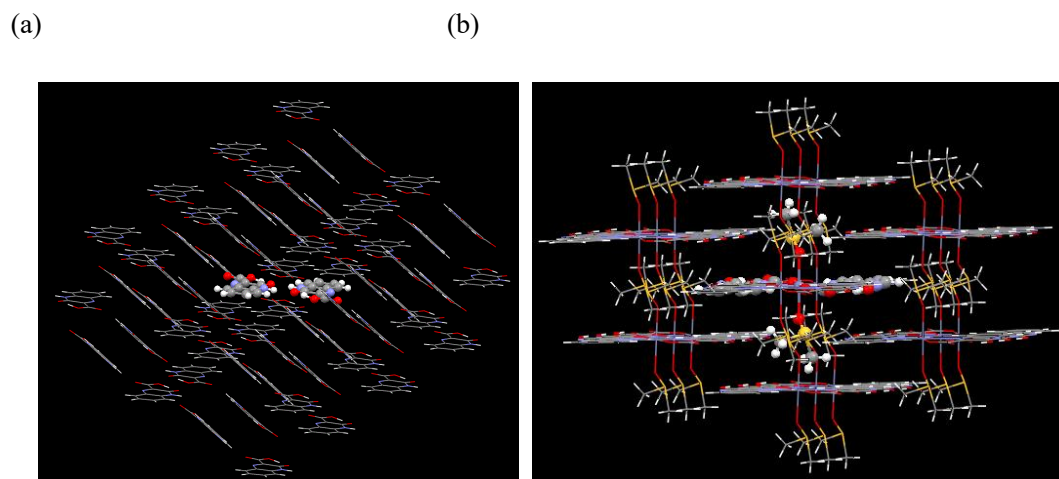


Figure 1. Cluster models for (a) lactam form dimer and (b) Zn-hqxc complex, containing 64 molecules ($2a+4b+2c$ axis) and 21 molecules ($2a+2.5b+c$ axis), respectively. Ball and stick molecules represent a high layer part and wireframe molecules represents a low layer.

For the Zn-hqxc complex, we calculated the IR spectrum of its monomer and compared it with the experimental results (Supporting Information). The result agrees well with the experiment. To observe the mechanical effects from the surrounding molecules, two-layer ONIOM calculations using 20 surrounding molecules were also performed, in which the coordinates of the surrounding molecules were fixed (Figure 1b). The change in bond distance with and without the surrounding molecules is 0.01-0.02 Å. Because the effects on bond distance changes due to surrounding molecules are negligible, we will hereafter consider only a monomer of the Zn-hqxc complex.

3.3.2. Excited states of hqxcH and Zn-hqxc complex in the ground state geometries

Before exploring the excited state geometries, we studied the excited states of hqxcH and the Zn-hqxc complex in

their ground state geometries. For hqxcH, in addition to the lactam dimer and monomer, the enol monomer is also considered in comparison to the Zn-hqxc complex because in the complex, the ligand is in its enol form. The absorption spectra and excited states of these molecules are shown in Figure 2.

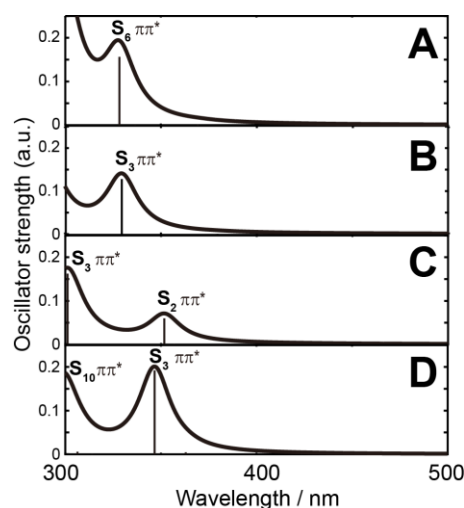


Figure 2. Simulated absorption spectra of excited states from 300 to 500 nm of A) lactam form dimer, B) lactam form monomer, C) enol form, and D) Zn-hqxc complex (M06/SDD (Zn), cc-pVDZ (other atoms)).

The excited states of hqxcH in the presented range are assigned to either $n\pi^*$ or $\pi\pi^*$ states (Supporting Information). The lowest energy absorption peak is observed at 330 nm (3.76 eV) for the lactam monomer which is in good agreement with the experimental absorption peak around 350 nm (3.54 eV).⁹⁶ Also, the lowest energy absorption peak is observed at 328 nm (3.78 eV) for the lactam dimer, indicating that the absorption spectra between the lactam dimer and monomer forms are almost unchanged when the intermolecular hydrogen bonding interactions exist.

The absorption peak for the enol monomer is at 352 nm (3.53 eV), lower than the lactam monomer by 0.23 eV. This energy difference can be attributed to the difference in HOMO energies, which is stabilized by 0.10 eV by the carboxylic acid in the lactam monomer. The absorption spectrum of enol is almost unchanged by the coordination of the zinc atom. Here, CC2/def-SVP calculations were carried out for Zn-hqxc complex at the equilibrium structure obtained by M06 to verify the accuracy of the excitation energies. The $\pi\pi^*$ excitation energy was calculated as 3.77 and 3.58 eV by CC2/def-SVP and M06/SDD (Zn), cc-pVDZ (other atoms), respectively, which supports qualitative accuracy of the present DFT calculations. The higher excitation energy calculated by CC2 is maybe a good tendency according to previous reports.⁹⁷

The excited states originate mainly from the hqxc ligand, in contrast to metal-centered (MC) or ligand-to-metal or metal-to-ligand charge transfer (LMCT/MLCT) excited states, which are widely observed in many metal complexes.^{98,99} This is because the d orbital of Zn(II) is totally filled and therefore an MC d-d transition or LMCT cannot occur. Moreover, filled d¹⁰ orbitals are very stable and the orbital energy is deep as shown in the density of states (DOS) in Figure 3, and therefore the MLCT excited state energy is much higher than LC for a Zn(II) complex.¹⁰⁰ The DOS also shows that the bond between Zn(II) and ligands has an ionic character, so the orbitals of hqxcH are marginally affected by the zinc atom, and the absorption spectra of enol and Zn-hqxc complexes are almost the same. Zn(II) complexes can take a high coordination number,¹⁰¹ which can be ascribed to the ionic nature of Zn(II). These results show that the effect of zinc atom on the excited states of Zn-hqxc complex is minor and would also be minor if the structural change from the lactam form to the enol form is caused via a coordination.

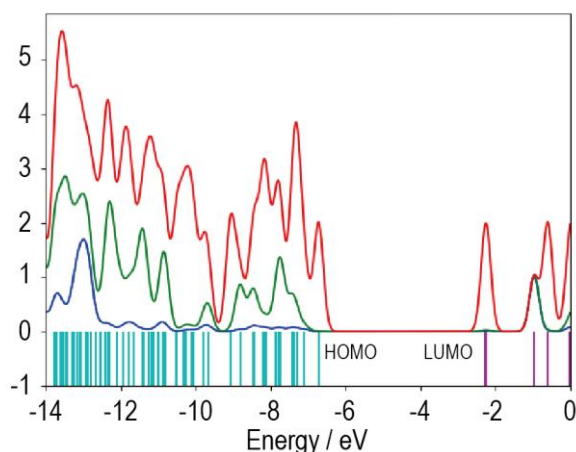
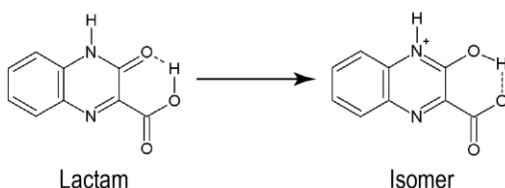


Figure 3. The density of state for Zn-hqxc complex at S_{0MIN} (M06/SDD (Zn), cc-pVDZ (other atoms)). Blue, green and red lines show the contribution from zinc atom, DMSO ligand and hqxc ligand, respectively. Light blue and purple vertical lines represent the occupied and virtual orbitals, respectively.

3.3.3. Excited states of the lactam form of hqxcH

The geometries of the lowest energy excited states of S_1 and T_1 are explored on the basis of the well-known Kasha's law¹⁰² to understand why the lactam form does not show ESIPT emission. In this section, we do not consider enol or keto forms because the position of the proton in these structures is too distant to be transferred, even in the excited state. We located one minimum structure in the ground state (S_{0MIN}), while one and three minima were obtained in the S_1 and T_1 states, respectively (S_{1MIN} and T_{1MIN}). S_{1MIN} of the lactam and isomer (Scheme 4) are assigned to $n\pi^*$. T_{1MIN} was found in both $n\pi^*$ and $\pi\pi^*$ excited states; in addition, an isomerized minimum was found in the $n\pi^*$ state. The emission energy for the S_1 state at S_{1MIN} (lactam, $n\pi^*$) in the lactam form was found to be 2.56 eV with a HOMO (n) to LUMO (π^*) transition. Because the oscillator strength is small (0.0003) for the S_{1MIN} (lactam, $n\pi^*$), this state may not be emissive. The emission energies at the three minima of the triplet states, T_{1MIN} (lactam, $n\pi^*$), T_{1MIN} (lactam, $\pi\pi^*$) in the lactam form and T_{1MIN} (isomer, $n\pi^*$) in the isomer form, are 2.12 eV, 1.95 eV, and 0.58 eV, respectively.



Scheme 4. Lactam isomerized to isomer via ESIPT

For the isomer form, we have obtained T_{1MIN} , but the energy gap with the S_0 state is small (~ 0.6 eV) compared to the other minima, suggesting a relatively fast relaxation. Since it has been reported that existence of local minima depends on the functionals in DFT calculations, especially for ESIPT molecules,^{103,104} we also performed geometry optimizations with various functionals (Supporting Information). We found S_{1MIN} of the isomer form using CAM-B3LYP. The energy gaps between S_1 or T_1 and S_0 states are small in the isomer form structure with all functionals used, which suggests a fast relaxation to the ground state. We did not obtain S_0 structures other than the S_{0MIN} , even with other functionals, indicating that if an isomerization occurs in the excited state from lactam to isomer, the hqxcH promptly relaxes back to lactam in the electronic ground state.

In the S_1 state, we also found S_{1TS} (lactam, $n\pi^*$). The IRC calculation was carried out from this TS. One side of

this IRC calculation goes toward an isomer form, which could not be fully optimized. This is perhaps because the S_1 and S_0 energy difference is less than 0.3 eV, suggesting that this structure is close to an S_1/S_0 conical intersection (CI). The barrier from S_{1MIN} (lactam, $n\pi^*$) to the CI is 0.07 eV, suggesting a fast relaxation to the ground state. The IRC paths revealed that ESIPT proceeds easily. This result coincides with the experimental result showing that hqxcH does not show ESIPT emission. Moreover, from the result of the energy profile along the IRC paths between S_{1TS} (lactam, $n\pi^*$) and S_{1MIN} (lactam, $n\pi^*$), the energy gap between the T_3 and the S_1 states becomes small as the structure approaches S_{1TS} (lactam, $n\pi^*$) (0.11 eV difference at the TS structure) (Figure 4). Intersystem crossing between the T_3 and S_1 states can occur during isomerization. From our calculations, therefore, phosphorescence is suggested to occur in the lactam monomer, although it was discussed to be fluorescence based on the experimental observation of a small Stokes shift ($3554\text{ cm}^{-1} \sim 0.44\text{ eV}$).⁷² The discrepancy may originate from neglecting π - π interactions in our calculations. This will be addressed in the future, as we did not consider π - π interactions in the present study because they were not expected to affect the ESIPT behavior.

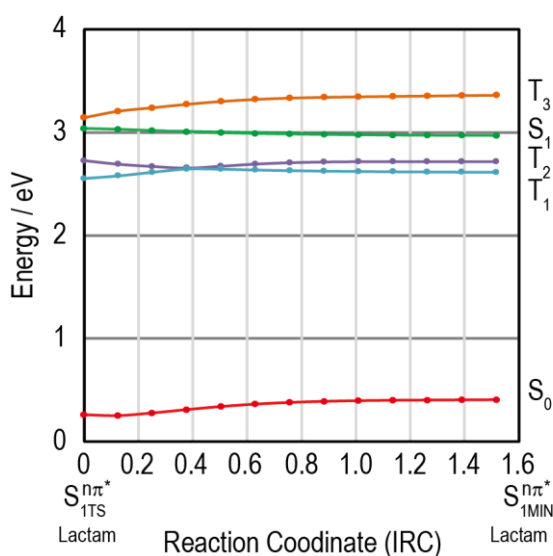


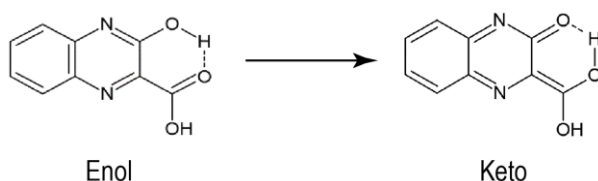
Figure 4. Potential energy curves along the IRC path from S_{1TS} (lactam, $n\pi^*$) to S_{1MIN} (lactam, $n\pi^*$) of lactam form monomer (M06/cc-pVDZ).

To analyze why the energy gap between the ground and excited states decreases in the isomer form, we analyze the electronic structure of the isomer. The n and π orbitals are destabilized in the S_1 and T_1 states via isomerization. These orbitals consist mainly of the carboxylate group. Upon isomerization, the carboxylic acid is changed to a

carboxylate, the latter of which has a negative charge, leading to the destabilization of the n and π orbitals. In contrast, the σ^* and π^* orbitals are localized to a N-H group, and the aromatic rings are stabilized due to a positive charge caused by the isomerization. A molecule having intramolecular charge polarization like this is called a zwitterion.

3.3.4. Excited states of enol and keto forms of hqxcH

Let us now investigate the excited states of the enol and keto forms of hqxcH, as these forms are observed in the Zn-hqxc complex. From geometry optimizations, only one minimum is obtained for the enol form ground state, while several minima in the enol and keto forms are obtained in the S_1 and T_1 states (Scheme 5). For these excited states, we found TSs connecting the enol and keto forms. The activation energy from S_{1MIN} (enol, $n\pi^*$) to S_{1MIN} (keto, $n\pi^*$) is 0.01 eV, and from S_{1MIN} (enol, $\pi\pi^*$) to S_{1MIN} (keto, $n\pi^*$) via two TSs is 0.04 eV. In contrast, T_{1MIN} (enol, $\pi\pi^*$) can also isomerize to T_{1MIN} (keto, $\pi\pi^*$) by an activation energy of 0.09 eV. These results mean that the enol form can isomerize to the keto form not only in the S_1 state, but also in the T_1 state.



Scheme 5. Enol isomerized to keto via ESIPT

S_{1MIN} (keto) and T_{1MIN} (keto) have substantial energy gaps relative to the S_0 state because there are no strong charge migrations, as found above. The results suggest that an ESIPT emission can occur if enol form of hqxcH exists. Regarding this, a quinoxalinone derivative containing $\text{CONHC}_{12}\text{H}_{25}$ was reported to show ESIPT emission.³⁵ Furthermore, a previous study reports that dual emission via ESIPT can occur if the Gibbs free energy difference between isomer (such as keto and enol) minima in the S_1 state is within 0.20 eV.⁵⁵ In our calculation, the Gibbs free energy difference was 0.26 eV between S_{1MIN} (enol, $\pi\pi^*$) and S_{1MIN} (keto, $n\pi^*$), which is larger than 0.20 eV. In contrast, the Gibbs free energy difference was 0.10 eV between S_{1MIN} (enol, $n\pi^*$) and S_{1MIN} (keto, $n\pi^*$). Moreover, after optimizing structures with B3LYP and CAM-B3LYP, S_{1MIN} (keto, $\pi\pi^*$) with a Gibbs free energy less than S_{1MIN} (enol, $\pi\pi^*$) by 0.06 eV was also obtained with B3LYP (0.01 eV with CAM-B3LYP). To explore the possibility of

intersystem crossing, we calculated the excited state energies for geometries interpolating S_{1MIN} (enol, $n\pi^*$) and T_{1MIN} (enol, $\pi\pi^*$) (Figure 5). From the energy diagram, the spin-forbidden transition via an intersystem crossing seems difficult because the crossing point energy between the T_3 and S_1 states is higher than S_{1MIN} (enol, $n\pi^*$) by 0.29 eV. However, the transition via an intersystem crossing to T_3 can occur around S_{1MIN} (enol, $\pi\pi^*$) due to a small energy gap of 0.06 eV (Figure 6). Thus, phosphorescence may occur in addition to fluorescence if these states exist.

From these results, we conclude that the structural change from lactam to enol, which occurs via coordination to the zinc atom, should be very important for ESIPT emission.

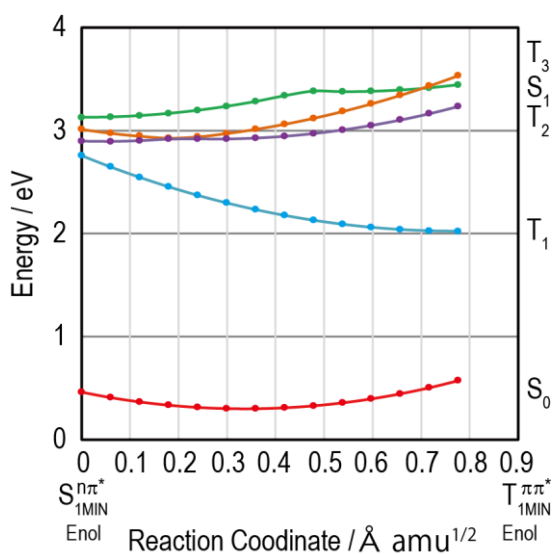


Figure 5. Potential energy curves along the linearly interpolated pathway which connects S_{1MIN} (enol, $n\pi^*$) and T_{1MIN} (enol, $\pi\pi^*$) of enol form optimized by TDDFT with M06/cc-pVDZ.

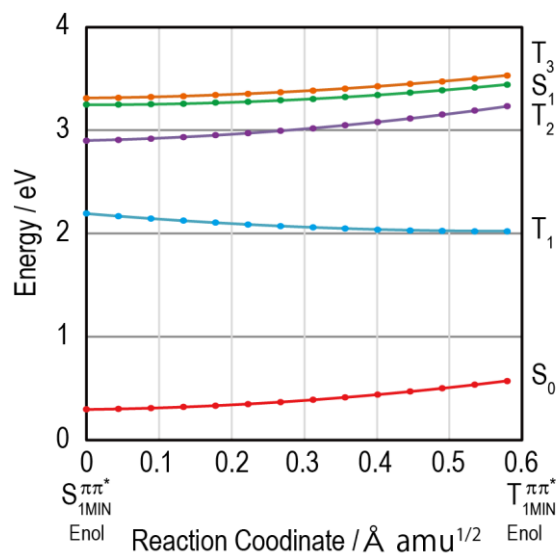
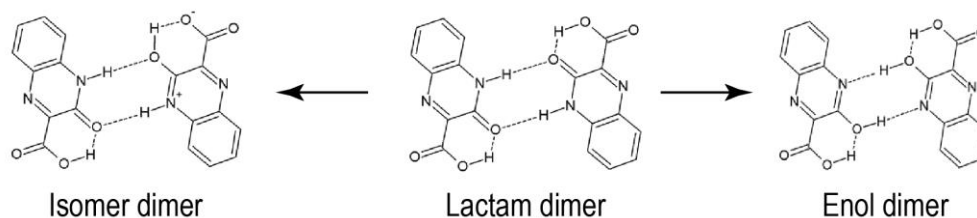


Figure 6. Potential energy curves along the linearly interpolated pathway which connects S_{1MIN} (enol, $\pi\pi^*$) and T_{1MIN} (enol, $\pi\pi^*$) of enol form optimized by TDDFT with M06/cc-pVDZ.

3.3.5. HqxcH dimer

For the lactam dimer, geometry optimizations give both lactam and enol forms in the ground and excited states (Supporting Information). In contrast to the monomer, a structural transition from lactam to enol could occur due to intermolecular hydrogen bonds, as shown in Scheme 6. The enol dimer is less stable than the lactam dimer by 0.6–0.9 eV in both the ground and excited states (Supporting Information). A geometry in which one of the hqxcHs isomerizes to have a carboxylate group in the excited states (isomer dimer, Scheme 6) also has close energy to the ground state. These results indicate that the photophysical property is less affected by dimerization. The lowest energy excited state is dominated more by the lactam form than by other forms.



Scheme 6. Lactam dimer isomerized to enol dimer and to isomer dimer

3.3.6. Role of zinc atom in Zn-hqxc complex with an ESIPT emission

To clarify the role of the zinc atom in the Zn-hqxc complex for ESIPT emission, we investigated excited states of the complex. The energy levels of obtained structures are summarized in Figure 7. In the ground state, only one minimum is obtained, which has an enol-enol form. Even when we began our geometry optimizations from keto-enol or keto-keto, the results yield the enol-enol geometry. For the S_1 state, two keto-enol structures were obtained having either $n\pi^*$ or $\pi\pi^*$ natures. For the T_1 state, three minima with enol-enol ($\pi\pi^*$), keto-enol ($\pi\pi^*$), and keto-keto ($\pi\pi^*$) forms were found when starting from various initial structures. The structures having either one or two ligands tautomerized to keto have higher S_0 energies compared to the enol-enol structure (Figure 7). This behavior is also found for the free hqxcH ligand and is consistent with other reports.^{49,54} Figure 8 plots the orbital energies for these structures, in which the orbital energy increases largely for the structures, including the tautomerized ligand, and the HOMO (π) increases while the LUMO (π^*) decreases. This is a natural phenomenon because tautomerization largely changes the molecular orbital (Figure 8).

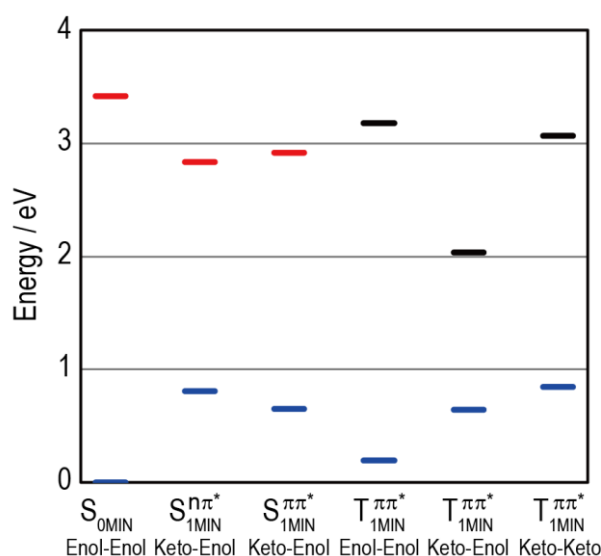


Figure 7. Relative energies of the ground and excited states of Zn-hqxc complex at each optimized structure (M06/SDD (Zn), cc-pVDZ (other atoms)). Zero represents the ground state energy. Blue, red, and black bars show the ground state, S_1 state, and T_1 state, respectively.

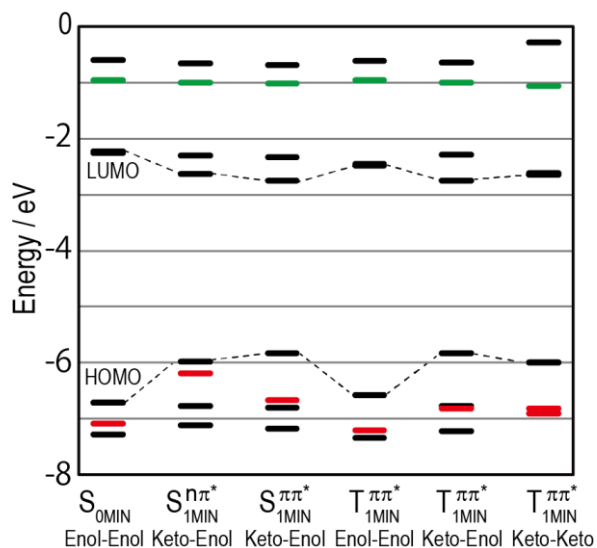


Figure 8. Orbital energies from HOMO-3 to LUMO+3 at each optimized structure of Zn-hqxc complex (M06/SDD (Zn), cc-pVDZ (other atoms)). Black, red, and green bars show π , π^* orbital, n orbital, and σ^* orbital, respectively. HOMO and LUMO are connected by dashed lines.

For the origin of the two experimental emissions at 2.35 eV and 2.58-2.92 eV, we compare calculated emission energies for the S_1 and T_1 states with experimental results.⁷² Table 1 shows the calculated 0-0 energy (= energy difference of S_0 minimum and S_1 (or T_1) minimum including zero-point vibrational energy) and emission energy. Theoretical emission energies were 2.03 eV with small oscillator strength (0.0006) for the S_1 state at S_{1MIN} (keto-enol, $n\pi^*$), 2.27 eV with large oscillator strength (0.0752) for the S_1 state at S_{1MIN} (keto-enol, $\pi\pi^*$), 2.99 eV for the T_1 state at T_{1MIN} (enol-enol, $\pi\pi^*$), 1.39 eV for the T_1 state at T_{1MIN} (keto-enol, $\pi\pi^*$), and 2.23 eV for the T_1 state at T_{1MIN} (keto-keto, $\pi\pi^*$). From comparisons of both energy and oscillator strength, the experimental emission at 2.35 eV seems to occur from S_{1MIN} (keto-enol, $\pi\pi^*$) and T_{1MIN} (keto-keto, $\pi\pi^*$). For the higher energy emission at 2.58-2.92 eV, T_{1MIN} (enol-enol, $\pi\pi^*$) is a reasonable choice in terms of the energy. While the present complex has been discussed to show only fluorescence,⁷² there exists Zn(II) complexes which show both fluorescence and phosphorescence in a solid state.¹⁰⁵⁻¹⁰⁸ From our computations, we would like to propose that the emission of the Zn-hqxc complex is caused by S_{1MIN} (keto-enol, $\pi\pi^*$), T_{1MIN} (enol-enol, $\pi\pi^*$), and T_{1MIN} (keto-keto, $\pi\pi^*$), therefore showing both fluorescence and phosphorescence.

Table 1. Theoretical 0-0 energy and emission energy at S_{1MIN} (keto-enol, $n\pi^*$), S_{1MIN} (keto-enol, $\pi\pi^*$), T_{1MIN} (enol-enol, $\pi\pi^*$), T_{1MIN} (keto-enol, $\pi\pi^*$), and T_{1MIN} (keto-keto, $\pi\pi^*$) (M06/SDD (Zn), cc-pVDZ (other atoms)). The 0-0 energy means the energy difference between S_0 minimum and S_1 (or T_1) minimum, including zero-point vibrational energy. The experimental 0-0 energy was estimated from the crossing point between excitation and emission spectra (450 nm).⁷²

	0-0 energy / eV	$E_{em.}$ / eV
S_{1MIN} (keto-enol, $n\pi^*$)	2.73	2.03
S_{1MIN} (keto-enol, $\pi\pi^*$)	2.82	2.27
T_{1MIN} (enol-enol, $\pi\pi^*$)	3.02	2.99
T_{1MIN} (keto-enol, $\pi\pi^*$)	1.96	1.39
T_{1MIN} (keto-keto, $\pi\pi^*$)	2.95	2.23
Experiment ⁷²	2.76	2.58-2.92, 2.35

To gain insight into the lifetime for these excited states, we examined the potential energy curves along the linearly-interpolated pathway which connects two S_{1MIN} (Supporting Information). The approximate energy barrier from S_{1MIN} (keto-enol, $n\pi^*$) to S_{1MIN} (keto-enol, $\pi\pi^*$) is 0.10 eV, and the reverse reaction, S_{1MIN} (keto-enol, $\pi\pi^*$) to S_{1MIN} (keto-enol, $n\pi^*$), is 0.01 eV. This small value indicates a fast transition between S_{1MIN} (keto-enol, $n\pi^*$) and S_{1MIN} (keto-enol, $\pi\pi^*$). In the T_1 state, we found the approximate energy barrier from T_{1MIN} (enol-enol, $\pi\pi^*$) to T_{1MIN} (keto-keto, $\pi\pi^*$) to be 0.24 eV, and the reverse reaction is 0.36 eV. Because there seems to be a substantial barrier, the structural change from T_{1MIN} (enol-enol, $\pi\pi^*$) to T_{1MIN} (keto-keto, $\pi\pi^*$) is expected to hardly occur. However, relaxations from T_{1MIN} (enol-enol, $\pi\pi^*$) and T_{1MIN} (keto-keto, $\pi\pi^*$) to T_{1MIN} (keto-enol, $\pi\pi^*$) can easily occur because there is no energy barrier. Considering these facts, the emission from T_{1MIN} (enol-enol, $\pi\pi^*$) and T_{1MIN} (keto-keto, $\pi\pi^*$) states can be weak, but surrounding molecules might suppress these relaxations and enhance emission from these states. The search for true transition states and therefore IRC calculations including surrounding molecules will be necessary to fully understand the lifetime. Also, SOC calculations and multiconfigurational wavefunctions are very important.^{61,62} To examine the possibility of spin-forbidden transition from singlet to triplet, we calculated SOC terms between singlet and triplet at three intersystem crossing points along the linearly-interpolated pathway which connects S_{0MIN} (enol-enol) and S_{1MIN} (keto-enol, $n\pi^*$) (Figure 9), at the SA-CASSCF/6-31G** level. The following formula is used to estimate SOC between S_1 and k th triplet states.

$$\text{SOC}_{k1} = \sqrt{\sum_u |\langle T_{k,u} | \hat{H}_{\text{SO}} | S_1 \rangle|^2} \quad (u = x, y, z)$$

To reproduce the excited-state character obtained by TDDFT calculations, we calculated three singlet and eight triplet states at the SA-CASSCF level, and assigned each excited state based on the electronic configurations. The calculated results are given in Table 2. The SOC at the first and second crossing points show negligible values, but the SOC at the third crossing point was calculated as 8.80 cm⁻¹ which possibly invokes a spin-forbidden transition from singlet to triplet during the tautomerization from enol-enol to keto-enol form.

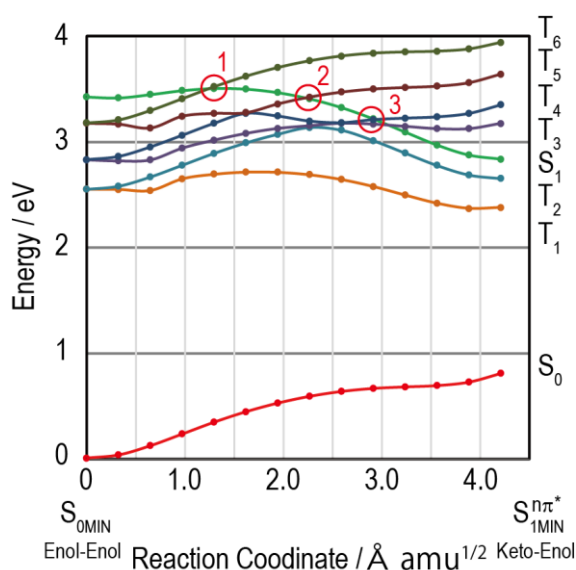


Figure 9. Potential energy curves along the linearly interpolated pathway which connects $S_{0\text{MIN}}$ (enol-enol, $\pi\pi^*$) and $S_{1\text{MIN}}$ (keto-enol, $n\pi^*$) of Zn-hqxc complex calculated by DFT and TDDFT (M06/SDD (Zn), cc-pVDZ (other atoms)). Three red circles with numbers show the crossing points between S_1 and triplet states where spin-orbit coupling is calculated.

Table 2. SOC between singlet and triplet states at three crossing points shown in Figure 9 calculated by SA-CASSCF/6-31G**.

Structure	target states	SOC / cm ⁻¹
1	S_1 and T_6	0.01
2	S_1 and T_5	0.03
3	S_1 and T_3	8.80
3	S_1 and T_4	0

These results demonstrate that the role of the zinc atom is to change the structure of hqxc ligand from lactam in its free state to enol upon the ligation, leaving the excited states of the ligand intact due to the closed 3d shell of Zn(II). The energetical comparisons suggest that the complex can show both phosphorescence and fluorescence via ESIPT leading to tautomerization from enol to keto form in the hqxc ligand. Other metal complexes with a potential ESIPT ligand, if any, whose photophysical properties are dominated by ligands (ligand centered, LC) like the Zn-hqxc complex can show ESIPT emission. Metal complexes with the same number of d-electrons as Zn(II), i.e., d^{10} metal complexes of Au(I), Ag(I), and Cu(I), have been known to show LC emission.^{109,110} For other metal atoms, we can choose cyclometalated Pt(II) and Ir(III) complexes because these cyclometalated complexes have very large d-d splitting, allowing their low-lying excited states to be LC.⁵⁹ A possible strategy for realizing ESIPT complexes is to use coinage metals or to prepare an ESIPT ligand that can cyclometalate to the above metal ions.

Before moving to the next section, let us mention the functional dependencies. Although the main conclusion on the role of the zinc atom is not affected, we observed that some of the results for excited state geometry optimizations depend on the functionals (Supporting Information). S_{1MIN} (keto-enol, $n\pi^*$) was obtained neither with CAM-B3LYP nor BHandHLYP. T_{1MIN} (enol-enol) and T_{1MIN} (keto-keto) were not fully obtained with CAM-B3LYP, and these structures continued to show small imaginary-number frequencies (smallest values are 24.5i, 5.5i cm^{-1}), which were ascribed to the DMSO ligands. Furthermore, the S_{1MIN} (enol-enol) and S_{1MIN} (keto-keto) forms minima could not be obtained with any of the used functionals, and these structures have one imaginary frequency ascribed to the antisymmetric frequency of the O-H bond to the keto-enol form.

3.3.7. IR frequency changes between ground and excited states: lactam and enol forms of hqxcH and Zn-hqxc complex

In general, an isomerization reaction can be detected by inspecting IR frequencies. For ESIPT, frequency changes (ex. N-H, O-H, C=O stretching) were measured in a previous report.⁴⁵ The IR spectra of hqxcH and the Zn-hqxc complex have not been obtained for their excited states. For future reference, we calculated IR spectra for hqxcH and the Zn-hqxc complex in their electronic excited states and compared with those in the electronic ground state. Figures

10-12 depict the IR spectra in the spectral range of 1500 to 4000 cm^{-1} , and Tables 3-5 show the representative IR frequencies (N-H, O-H, C=O stretching) of each optimized structure.

Figure 10 and Table 3 summarize results concerning the lactam hqxcH monomer. The O-H stretching frequency varies in the excited states. The lower O-H binding energy suggests easier ESIPT. The C=O stretching frequency is almost constant in position for lactam form but shifts for the isomer form. The C=O stretching in the $\mathbf{T}_{1\text{MIN}}$ (isomer, $n\pi^*$) is at 1644 cm^{-1} , which corresponds to the carboxylate group. The IR frequencies assigned to C-H and N-H stretchings do not largely change. The bond distances of C-H and N-H are also relatively unchanged compared to the other bonds in the excited states.

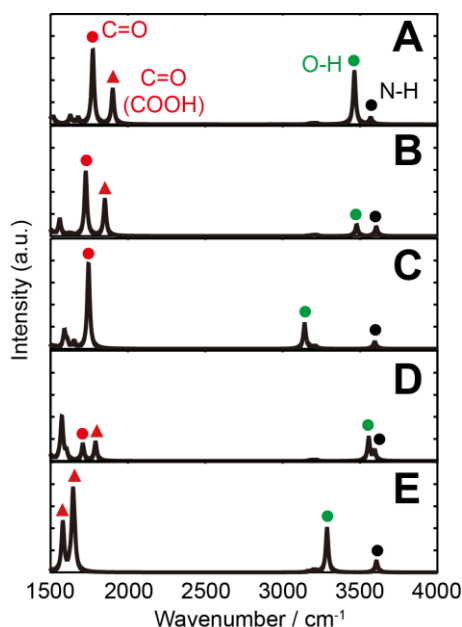


Figure 10. IR spectra for optimized structures of lactam form from 1500 to 4000 cm^{-1} (M06/cc-pVDZ). A) $\mathbf{S}_{0\text{MIN}}$ (lactam), B) $\mathbf{S}_{1\text{MIN}}$ (lactam, $n\pi^*$), C) $\mathbf{T}_{1\text{MIN}}$ (lactam, $n\pi^*$), D) $\mathbf{T}_{1\text{MIN}}$ (lactam, $\pi\pi^*$), and E) $\mathbf{T}_{1\text{MIN}}$ (isomer, $n\pi^*$).

Table 3. Selected IR frequencies after optimization for $\mathbf{S}_{0\text{MIN}}$ (lactam), $\mathbf{S}_{1\text{MIN}}$ (lactam, $n\pi^*$), $\mathbf{T}_{1\text{MIN}}$ (lactam, $n\pi^*$), $\mathbf{T}_{1\text{MIN}}$ (lactam, $\pi\pi^*$), and $\mathbf{T}_{1\text{MIN}}$ (isomer, $n\pi^*$) (M06/cc-pVDZ).

Optimized structure	N-H / cm^{-1}	O-H / cm^{-1}	C=O / cm^{-1}
$\mathbf{S}_{0\text{MIN}}$ (lactam)	3569	3464	1902, 1773
$\mathbf{S}_{1\text{MIN}}$ (lactam, $n\pi^*$)	3605	3478	1851, 1727
$\mathbf{T}_{1\text{MIN}}$ (lactam, $n\pi^*$)	3595	3141	1745
$\mathbf{T}_{1\text{MIN}}$ (lactam, $\pi\pi^*$)	3594	3556	1790, 1708
$\mathbf{T}_{1\text{MIN}}$ (isomer, $n\pi^*$)	3606	3287	1644, 1580

Next, we focus on the keto and enol hqxcH forms. As summarized in Figure 11 and Table 4, the O-H and C=O stretching frequencies are related to an ESIPT red-shift in the excited states compared to the ground state. The variation of O-H frequency of the COOH group, which is irrespective to the ESIPT, is very small. The frequency change in the S_{1MIN} (enol, $n\pi^*$) is larger than that in S_{1MIN} (enol, $\pi\pi^*$) and T_{1MIN} (enol, $\pi\pi^*$) because the $n\pi^*$ transition concerns these bonds. The largest red-shifts of the O-H frequency are found for S_{1MIN} (enol, $n\pi^*$), suggesting that O-H bond breaking occurs the most readily. This is consistent with our above finding from the IRC results, that ESIPT from this state occurs most readily.

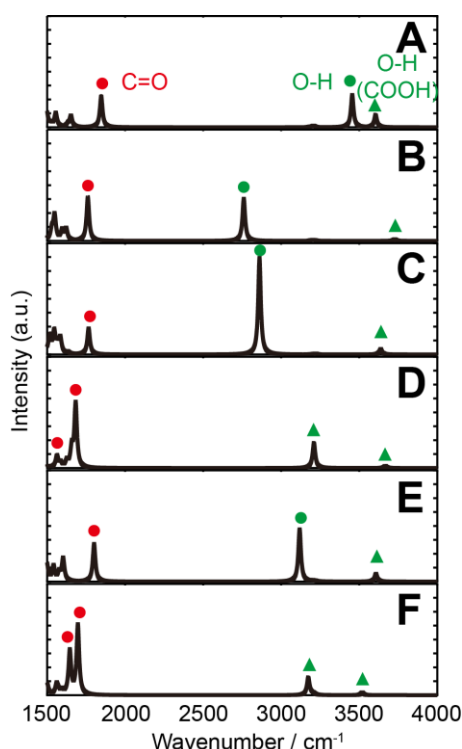


Figure 11. IR spectra for optimized structures of enol form from 1500 to 4000 cm^{-1} (M06/cc-pVDZ). A) S_{0MIN} (enol), B) S_{1MIN} (enol, $n\pi^*$), C) S_{1MIN} (enol, $\pi\pi^*$), D) S_{1MIN} (keto, $\pi\pi^*$), E) T_{1MIN} (enol, $\pi\pi^*$), and F) T_{1MIN} (keto, $\pi\pi^*$).

Table 4. Selected IR frequencies after optimization for the $S_{0\text{MIN}}$ (enol), $S_{1\text{MIN}}$ (enol, $n\pi^*$), $S_{1\text{MIN}}$ (enol, $\pi\pi^*$), $S_{1\text{MIN}}$ (keto, $\pi\pi^*$), $T_{1\text{MIN}}$ (enol, $\pi\pi^*$), and $T_{1\text{MIN}}$ (keto, $\pi\pi^*$) (M06/cc-pVDZ).

Optimized structure	O-H / cm^{-1}	C=O / cm^{-1}
$S_{0\text{MIN}}$ (enol)	3605, 3455	1846
$S_{1\text{MIN}}$ (enol, $n\pi^*$)	3727, 2760	1761
$S_{1\text{MIN}}$ (enol, $\pi\pi^*$)	3637, 2861	1766
$S_{1\text{MIN}}$ (keto, $n\pi^*$)	3667, 3210	1683, 1658, 1563
$T_{1\text{MIN}}$ (enol, $\pi\pi^*$)	3607, 3118	1801
$T_{1\text{MIN}}$ (keto, $\pi\pi^*$)	3519, 3173	1697, 1645, 1596

Let us focus on the Zn-hqxc complex. The red-shift of the O-H stretching frequency compared with the ground state is larger for $T_{1\text{MIN}}$ (enol-enol, $\pi\pi^*$) and $T_{1\text{MIN}}$ (keto-keto, $\pi\pi^*$) than for the others (Figure 12, Table 5), suggesting that $T_{1\text{MIN}}$ (enol-enol, $\pi\pi^*$) and $T_{1\text{MIN}}$ (keto-keto, $\pi\pi^*$) can easily tautomerize to $T_{1\text{MIN}}$ (keto-enol, $\pi\pi^*$). This fact also coincides with the energy profiles of the linearly interpolated results, which show no energy barrier (Supporting Information). The IR frequency ascribed to the DMSO ligand is retained in the excited states because the lowest energy excited states are rather localized to the hqxc ligands.

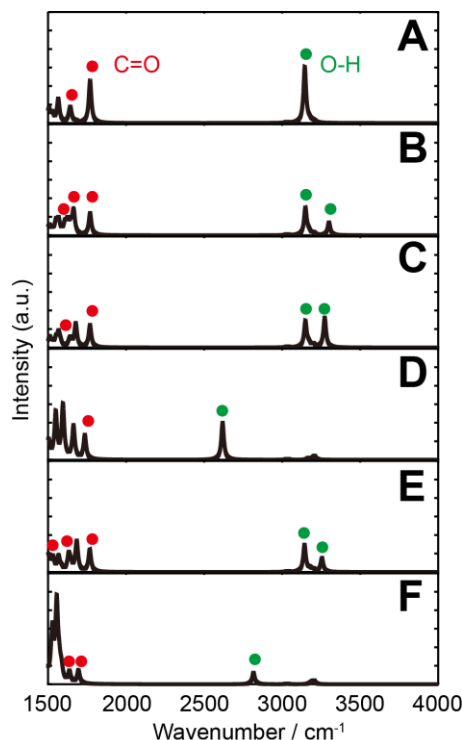


Figure 12. IR spectra for optimized structures of Zn-hqxc complex from 1500 to 4000 cm^{-1} (M06/SDD (Zn), cc-pVDZ (other atoms)). A) $S_{0\text{MIN}}$ (enol-enol), B) $S_{1\text{MIN}}$ (keto-enol, $n\pi^*$), C) $S_{1\text{MIN}}$ (keto-enol, $\pi\pi^*$), D) $T_{1\text{MIN}}$ (enol-enol, $\pi\pi^*$), E) $T_{1\text{MIN}}$ (keto-enol, $\pi\pi^*$), and F) $T_{1\text{MIN}}$ (keto-keto, $\pi\pi^*$).

Table 5. Selected IR frequencies after optimization for the $S_{0\text{MIN}}$ (enol-enol), $S_{1\text{MIN}}$ (keto-enol, $n\pi^*$), $S_{1\text{MIN}}$ (keto-enol, $\pi\pi^*$), $T_{1\text{MIN}}$ (enol-enol, $\pi\pi^*$), and $T_{1\text{MIN}}$ (keto-enol, $\pi\pi^*$) (M06/SDD (Zn), cc-pVDZ (other atoms)).

Optimized structure	O-H / cm^{-1} (enol)	O-H / cm^{-1} (keto)	C=O / cm^{-1} (enol)	C=O / cm^{-1} (keto)
$S_{0\text{MIN}}$ (enol-enol)	3145		1769, 1644	
$S_{1\text{MIN}}$ (keto-enol, $n\pi^*$)	3149	3300	1769, 1646	1664, 1625, 1609
$S_{1\text{MIN}}$ (keto-enol, $\pi\pi^*$)	3149	3273	1769, 1646	1635, 1513
$T_{1\text{MIN}}$ (enol-enol, $\pi\pi^*$)	2618		1736	
$T_{1\text{MIN}}$ (keto-enol, $\pi\pi^*$)	3143	3255	1767, 1646	1632, 1586, 1533
$T_{1\text{MIN}}$ (keto-keto, $\pi\pi^*$)		2816		1695, 1637, 1586, 1572

3.4. CONCLUDING REMARKS

We have carried out DFT and TDDFT calculations for hqxcH and the Zn-hqxc complex in the gas phase to investigate their excited states and emission mechanisms, with special attention to ESIPT and the role of the zinc

atom. Tautomerization from the lactam form leads to a small energy gap between the S_1 (or T_1) and S_0 states due to the carboxylate group, suggesting the existence of a conical intersection that can cause fast relaxation to the ground state. This result coincides with the experimental results showing that hqxcH does not exhibit ESIPT emission. In the complex, the structural change from the lactam form to the enol form is induced via coordination to zinc atom. This structural change in the ligand upon coordination plays a vital role for the ESIPT emission of the complex which is not observed in the free ligand. From our results, the ESIPT emission of the Zn-hqxc complex can be both fluorescence and phosphorescence. Although this is rare, the phosphorescence could be enhanced by the non-negligible spin-orbit effect. As determined by analyzing the excited states, the excited states are ligand-centered due to the closed 3d shell of Zn(II), indicating that this is one of the key ingredients in developing new ESIPT complexes.

3.5. Supporting Information

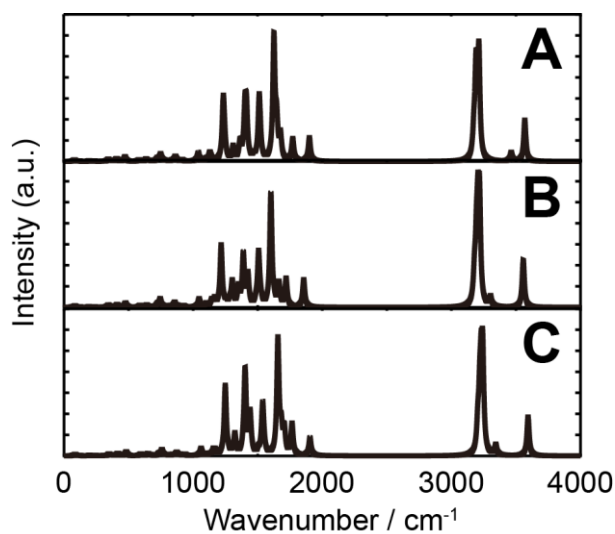


Figure S1. Raman spectra of lactam form at $S_{0\text{MIN}}$ calculated by DFT with various functionals and cc-pVDZ: A) M06, B) B3LYP, C) CAM-B3LYP.

Table S1. Selected Raman frequencies after optimization for lactam form at $S_{0\text{MIN}}$ with various functionals and cc-pVDZ, with experimental values.

	N-H / cm^{-1}	O-H / cm^{-1}	C=O / cm^{-1}
M06	3569	3464	1902, 1773
B3LYP	3557	3303	1856, 1720,
CAM-B3LYP	3594	3344	1905, 1766
Experimental ¹	3084	3009	1839, 1745

1) S. Badoğlu *et. al.*, *Spectrochim. Acta Part A Mol. Biomol. Spectrosc.* **2013**, 101, 14–21.

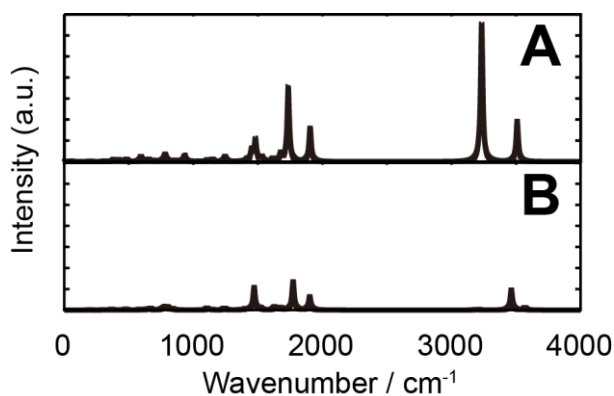


Figure S2. Calculated IR spectra of lactam form A) dimer and B) monomer at S_{0MIN} from 0 to 4000 cm^{-1} (M06/cc-pVDZ).

Table S2. Selected IR frequencies after optimization for lactam form dimer and monomer at S_{0MIN} (M06/cc-pVDZ) with experimental values.

	N-H / cm^{-1}	O-H / cm^{-1}	C=O / cm^{-1}
S_{0MIN} (dimer)	3234, 3192, 3186, 3184	3511, 3509	1906, 1905, 1735, 1713, 1617, 1612
S_{0MIN} (monomer)	3569	3464	1902, 1773
Experimental ¹	3077	3012	1837, 1737

1) S. Badoğlu *et. al.*, *Spectrochim. Acta Part A Mol. Biomol. Spectrosc.* **2013**, 101, 14–21.

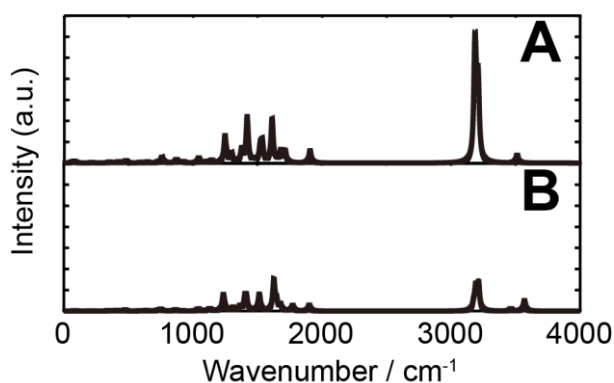


Figure S3. Calculated Raman spectra of lactam form A) dimer and B) monomer at S_{0MIN} from 0 to 4000 cm^{-1} (M06/cc-pVDZ).

Table S3. Selected Raman frequencies after optimization for lactam form dimer and monomer at S_{0MIN} (M06/cc-pVDZ), with experimental values.

	N-H / cm^{-1}	O-H / cm^{-1}	C=O / cm^{-1}
S_{0MIN} (dimer)	3234, 3192, 3186, 3184	3511, 3509	1906, 1905, 1735, 1713, 1617, 1612
S_{0MIN} (monomer)	3569	3464	1902, 1773
Experimental ¹	3084	3009	1839, 1745

1) S. Badoğlu *et al.*, *Spectrochim. Acta Part A Mol. Biomol. Spectrosc.* **2013**, 101, 14–21.

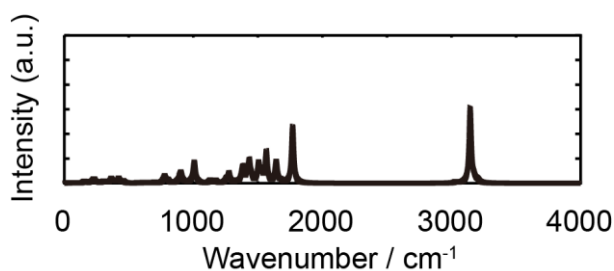


Figure S4. Calculated IR spectrum of Zn-hqxc complex at S_{0MIN} from 0 to 4000 cm^{-1} (M06/SDD (Zn), cc-pVDZ (other atoms)).

Table S4. Selected IR frequencies after optimization for Zn-hqxc complex at S_{0MIN} (M06/SDD (Zn), cc-pVDZ (other atoms)), with experimental values.

	O-H / cm^{-1}	C=O / cm^{-1}
S_{0MIN} (monomer)	3145	1769, 1644
Experimental ²	3447	~ 1700

2) K.-I. Sakai, *et al.*, *Dalton Trans.* **2010**, 39 (8), 1989-1995.

Table S5. Excitation energy, oscillator strength, and details of the transitions and their contributions for lactam form dimer (M06/cc-pVDZ).

Excited state	Excitation energy / eV	Oscillator strength	Transitions	Contribution / %
T ₁	2.61		HOMO-5 – LUMO ($\pi \rightarrow \pi^*$)	20.7
			HOMO-4 – LUMO+1 ($\pi \rightarrow \pi^*$)	20.4
			HOMO-1 – LUMO+1 ($\pi \rightarrow \pi^*$)	24.1
			HOMO – LUMO ($\pi \rightarrow \pi^*$)	26.9
T ₂	2.61		HOMO-5 – LUMO+1 ($\pi \rightarrow \pi^*$)	20.5
			HOMO-4 – LUMO ($\pi \rightarrow \pi^*$)	20.8
			HOMO-1 – LUMO ($\pi \rightarrow \pi^*$)	25.4
			HOMO – LUMO+1 ($\pi \rightarrow \pi^*$)	25.3
T ₃	2.98		HOMO-7 – LUMO+1 ($n \rightarrow \pi^*$)	24.7
			HOMO-6 – LUMO ($n \rightarrow \pi^*$)	17.9
			HOMO-3 – LUMO+1 ($n \rightarrow \pi^*$)	13.4
			HOMO-2 – LUMO ($n \rightarrow \pi^*$)	37.1
T ₄	2.98		HOMO-7 – LUMO ($n \rightarrow \pi^*$)	26.5
			HOMO-6 – LUMO+1 ($n \rightarrow \pi^*$)	16.8
			HOMO-3 – LUMO ($n \rightarrow \pi^*$)	14.5
			HOMO-2 – LUMO+1 ($n \rightarrow \pi^*$)	35.2
T ₅	3.00		HOMO-5 – LUMO ($\pi \rightarrow \pi^*$)	20.6
			HOMO-5 – LUMO+4 ($\pi \rightarrow \pi^*$)	2.9
			HOMO-4 – LUMO+1 ($\pi \rightarrow \pi^*$)	20.7
			HOMO-4 – LUMO+5 ($\pi \rightarrow \pi^*$)	2.8
			HOMO-1 – LUMO+1 ($\pi \rightarrow \pi^*$)	20.3
			HOMO-1 – LUMO+3 ($\pi \rightarrow \pi^*$)	2.2
			HOMO – LUMO ($\pi \rightarrow \pi^*$)	26.0
			HOMO – LUMO+2 ($\pi \rightarrow \pi^*$)	2.1
S ₁	3.35	0.0000	HOMO-7 – LUMO+1 ($n \rightarrow \pi^*$)	12.0
			HOMO-6 – LUMO ($n \rightarrow \pi^*$)	6.9
			HOMO-3 – LUMO+1 ($n \rightarrow \pi^*$)	25.0
			HOMO-2 – LUMO ($n \rightarrow \pi^*$)	53.7
S ₂	3.36	0.0011	HOMO-7 – LUMO ($n \rightarrow \pi^*$)	12.8
			HOMO-6 – LUMO+1 ($n \rightarrow \pi^*$)	6.0
			HOMO-3 – LUMO ($n \rightarrow \pi^*$)	28.1
			HOMO-2 – LUMO+1 ($n \rightarrow \pi^*$)	50.7
S ₃	3.68	0.0000	HOMO-7 – LUMO+1 ($n \rightarrow \pi^*$)	24.8
			HOMO-6 – LUMO ($n \rightarrow \pi^*$)	48.0

			HOMO-3 – LUMO+1 ($n \rightarrow \pi^*$)	20.1
			HOMO-2 – LUMO ($n \rightarrow \pi^*$)	3.1
S ₄	3.69	0.0001	HOMO-7 – LUMO ($n \rightarrow \pi^*$)	27.6
			HOMO-6 – LUMO+1 ($n \rightarrow \pi^*$)	45.3
			HOMO-3 – LUMO ($n \rightarrow \pi^*$)	20.7
			HOMO-2 – LUMO+1 ($n \rightarrow \pi^*$)	2.4
S ₅	3.71	0.0000	HOMO-5 – LUMO ($\pi \rightarrow \pi^*$)	2.6
			HOMO-4 – LUMO+1 ($\pi \rightarrow \pi^*$)	2.5
			HOMO-1 – LUMO+1 ($\pi \rightarrow \pi^*$)	31.5
			HOMO – LUMO ($\pi \rightarrow \pi^*$)	60.5

Table S6. Excitation energy, oscillator strength, and details of the transitions and their contributions for lactam form monomer (M06/cc-pVDZ).

Excited state	Excitation energy / eV	Oscillator strength	Transitions	Contribution / %
T ₁	2.56		HOMO-7 – LUMO ($\pi \rightarrow \pi^*$)	2.2
			HOMO-2 – LUMO ($\pi \rightarrow \pi^*$)	29.2
			HOMO – LUMO ($\pi \rightarrow \pi^*$)	63.9
			HOMO – LUMO+1 ($\pi \rightarrow \pi^*$)	2.3
T ₂	2.92		HOMO-5 – LUMO ($n \rightarrow \pi^*$)	3.3
			HOMO-3 – LUMO ($n \rightarrow \pi^*$)	34.5
			HOMO-1 – LUMO ($n \rightarrow \pi^*$)	57.6
T ₃	3.13		HOMO-2 – LUMO ($\pi \rightarrow \pi^*$)	52.3
			HOMO-2 – LUMO+2 ($\pi \rightarrow \pi^*$)	6.5
			HOMO – LUMO ($\pi \rightarrow \pi^*$)	33.6
			HOMO – LUMO+1 ($\pi \rightarrow \pi^*$)	4.8
S ₁	3.27	0.0005	HOMO-3 – LUMO ($n \rightarrow \pi^*$)	16.1
			HOMO-1 – LUMO ($n \rightarrow \pi^*$)	81.1
T ₄	3.39		HOMO-3 – LUMO ($n \rightarrow \pi^*$)	55.2
			HOMO-1 – LUMO ($n \rightarrow \pi^*$)	37.0
			HOMO-1 – LUMO+3 ($n \rightarrow \pi^*$)	2.6
S ₂	3.63	0.0000	HOMO-3 – LUMO ($n \rightarrow \pi^*$)	79.6
			HOMO-1 – LUMO ($n \rightarrow \pi^*$)	16.1
S ₃	3.76	0.1277	HOMO-2 – LUMO ($\pi \rightarrow \pi^*$)	4.9
			HOMO-2 – LUMO+1 ($\pi \rightarrow \pi^*$)	2.6
			HOMO – LUMO ($\pi \rightarrow \pi^*$)	91.9
T ₅	3.97		HOMO-4 – LUMO ($\pi \rightarrow \pi^*$)	3.1

			HOMO-2 – LUMO ($\pi \rightarrow \pi^*$)	11.1
			HOMO-2 – LUMO+1 ($\pi \rightarrow \pi^*$)	5.2
			HOMO-2 – LUMO+2 ($\pi \rightarrow \pi^*$)	7.1
			HOMO – LUMO+1 ($\pi \rightarrow \pi^*$)	64.7
S ₄	4.26	0.1689	HOMO-2 – LUMO ($\pi \rightarrow \pi^*$)	88.0
			HOMO – LUMO ($\pi \rightarrow \pi^*$)	4.4
			HOMO – LUMO+1 ($\pi \rightarrow \pi^*$)	6.3
S ₅	4.98	0.0071	HOMO-4 – LUMO ($\pi \rightarrow \pi^*$)	97.6

Table S7. Excitation energy, oscillator strength, and details of the transitions and their contributions for enol form (M06/cc-pVDZ).

Excited state	Excitation energy / eV	Oscillator strength	Transitions	Contribution / %
T ₁	2.50		HOMO-1 – LUMO ($\pi \rightarrow \pi^*$)	11.6
			HOMO-1 – LUMO+2 ($\pi \rightarrow \pi^*$)	3.1
			HOMO – LUMO ($\pi \rightarrow \pi^*$)	76.0
			HOMO – LUMO+1 ($\pi \rightarrow \pi^*$)	6.8
T ₂	2.84		HOMO-1 – LUMO ($\pi \rightarrow \pi^*$)	76.1
			HOMO – LUMO ($\pi \rightarrow \pi^*$)	17.9
T ₃	3.17		HOMO-2 – LUMO ($n \rightarrow \pi^*$)	95.2
S ₁	3.47	0.0011	HOMO-2 – LUMO ($n \rightarrow \pi^*$)	98.3
S ₂	3.53	0.0601	HOMO-1 – LUMO+1 ($\pi \rightarrow \pi^*$)	2.3
			HOMO – LUMO ($\pi \rightarrow \pi^*$)	95.9
T ₄	3.93		HOMO-1 – LUMO ($\pi \rightarrow \pi^*$)	7.3
			HOMO-1 – LUMO+1 ($\pi \rightarrow \pi^*$)	3.1
			HOMO – LUMO ($\pi \rightarrow \pi^*$)	3.9
			HOMO – LUMO+1 ($\pi \rightarrow \pi^*$)	80.9
S ₃	4.12	0.1624	HOMO-1 – LUMO ($\pi \rightarrow \pi^*$)	87.0
			HOMO – LUMO+1 ($\pi \rightarrow \pi^*$)	10.0
T ₅	4.29		HOMO-3 – LUMO ($n \rightarrow \pi^*$)	86.5
			HOMO-2 – LUMO+1 ($n \rightarrow \pi^*$)	3.3
			HOMO-2 – LUMO+3 ($n \rightarrow \pi^*$)	3.5
S ₄	4.58	0.0000	HOMO-3 – LUMO ($n \rightarrow \pi^*$)	93.8
S ₅	5.11	0.0001	HOMO-2 – LUMO+1 ($n \rightarrow \pi^*$)	94.3

Table S8. Excitation energy, oscillator strength, and details of the transitions and their contributions for Zn-hqxc complex (M06/SDD (Zn), cc-pVDZ (other atoms)).

Excited state	Excitation energy / eV	Oscillator strength	Transitions	Contribution / %
T ₁	2.54		HOMO-4 – LUMO ($\pi \rightarrow \pi^*$)	3.4
			HOMO-3 – LUMO+1 ($\pi \rightarrow \pi^*$)	2.8
			HOMO-1 – LUMO+1 ($\pi \rightarrow \pi^*$)	40.2
			HOMO-1 – LUMO+4 ($\pi \rightarrow \pi^*$)	2.6
			HOMO – LUMO ($\pi \rightarrow \pi^*$)	41.2
			HOMO – LUMO+3 ($\pi \rightarrow \pi^*$)	2.7
T ₂	2.54		HOMO-4 – LUMO+1 ($\pi \rightarrow \pi^*$)	3.5
			HOMO-3 – LUMO ($\pi \rightarrow \pi^*$)	2.8
			HOMO-1 – LUMO ($\pi \rightarrow \pi^*$)	41.0
			HOMO-1 – LUMO+3 ($\pi \rightarrow \pi^*$)	2.7
			HOMO – LUMO+1 ($\pi \rightarrow \pi^*$)	40.4
			HOMO – LUMO+4 ($\pi \rightarrow \pi^*$)	2.6
T ₃	2.82		HOMO-5 – LUMO+1 ($n \rightarrow \pi^*$)	9.1
			HOMO-4 – LUMO ($\pi \rightarrow \pi^*$)	38.0
			HOMO-3 – LUMO+1 ($\pi \rightarrow \pi^*$)	29.1
			HOMO-1 – LUMO+1 ($\pi \rightarrow \pi^*$)	6.4
			HOMO – LUMO ($\pi \rightarrow \pi^*$)	6.6
T ₄	2.82		HOMO-5 – LUMO ($n \rightarrow \pi^*$)	9.3
			HOMO-4 – LUMO+1 ($\pi \rightarrow \pi^*$)	37.2
			HOMO-3 – LUMO ($\pi \rightarrow \pi^*$)	29.6
			HOMO-1 – LUMO ($\pi \rightarrow \pi^*$)	6.9
			HOMO – LUMO+1 ($\pi \rightarrow \pi^*$)	6.0
T ₅	3.17		HOMO-9 – LUMO+1 ($n \rightarrow \pi^*$)	2.1
			HOMO-5 – LUMO+1 ($n \rightarrow \pi^*$)	25.7
			HOMO-3 – LUMO+1 ($\pi \rightarrow \pi^*$)	8.1
			HOMO-2 – LUMO ($n \rightarrow \pi^*$)	58.1
S ₁	3.42	0.0043	HOMO-5 – LUMO+1 ($n \rightarrow \pi^*$)	24.7
			HOMO-3 – LUMO+1 ($\pi \rightarrow \pi^*$)	8.0
			HOMO-2 – LUMO ($n \rightarrow \pi^*$)	62.3
S ₂	3.42	0.0000	HOMO-5 – LUMO ($n \rightarrow \pi^*$)	26.0
			HOMO-3 – LUMO ($\pi \rightarrow \pi^*$)	8.9
			HOMO-2 – LUMO+1 ($n \rightarrow \pi^*$)	60.0
S ₃	3.58	0.1922	HOMO-1 – LUMO+1 ($\pi \rightarrow \pi^*$)	44.9
			HOMO – LUMO ($\pi \rightarrow \pi^*$)	50.2

S ₄	3.59	0.0000	HOMO-1 – LUMO ($\pi \rightarrow \pi^*$)	50.9
			HOMO – LUMO+1 ($\pi \rightarrow \pi^*$)	44.1
S ₅	3.95	0.0004	HOMO-1 – LUMO+1 ($\pi \rightarrow \pi^*$)	52.5
			HOMO – LUMO ($\pi \rightarrow \pi^*$)	46.2

Table S9. The emission energy, oscillator strength, and major transition at minimum structures obtained by geometry optimizations for lactam form monomer obtained by DFT with various functionals and cc-pVDZ.

Functional	Minimum structure	Emission energy / eV	Oscillator strength	Major transitions	Contribution / %
M06	S _{1MIN} (lactam, $n\pi^*$)	2.56	0.0003	HOMO – LUMO	93.7
	T _{1MIN} (lactam, $n\pi^*$)	2.12		HOMO – LUMO	
	T _{1MIN} (lactam, $\pi\pi^*$)	1.95		HOMO – LUMO	
	T _{1MIN} (isomer, $n\pi^*$)	0.58		HOMO – LUMO	
B3LYP	T _{1MIN} (lactam, $\pi\pi^*$)	2.03		HOMO – LUMO	
	T _{1MIN} (isomer, $n\pi^*$)	0.57		HOMO – LUMO	
CAM-B3LYP	S _{1MIN} (lactam, $n\pi^*$)	2.83	0.0004	HOMO-1 – LUMO	87.3
	S _{1MIN} (isomer, $n\pi^*$)	0.76	0.0000	HOMO – LUMO	96.9
	T _{1MIN} (lactam, $n\pi^*$)	1.81		HOMO – LUMO	
	T _{1MIN} (lactam, $\pi\pi^*$)	1.96		HOMO – LUMO	
	T _{1MIN} (isomer, $n\pi^*$)	0.61		HOMO – LUMO	

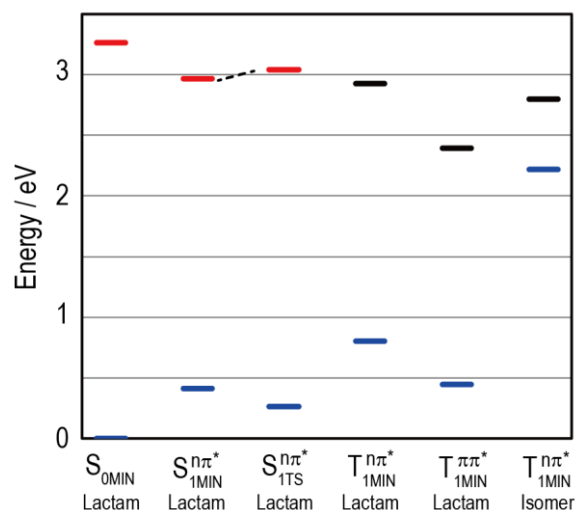


Figure S5. Relative energies of the ground and excited states of lactam form at each optimized structure (M06/cc-pVDZ). Zero represents the ground state energy. Blue, red, and black bars show the ground state, S₁ state, and T₁ state, respectively. IRC path is connected by the dashed line.

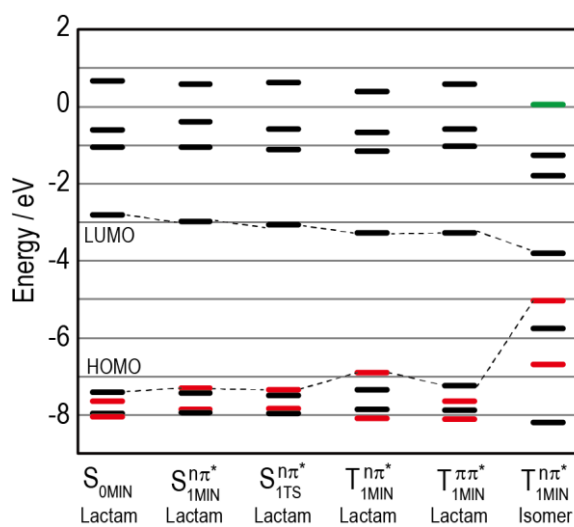


Figure S6. Orbital energies from HOMO-3 to LUMO+3 at each optimized structure of lactam form (M06/cc-pVDZ). Black, red, and green bars show π and π^* , n, and σ^* orbitals, respectively. HOMO and LUMO are connected by dashed lines.

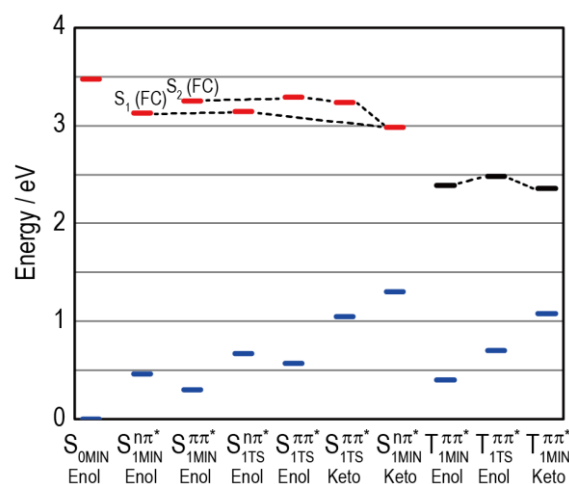


Figure S7. Relative energies of the ground and excited states of enol form at each optimized structure (M06/cc-pVDZ). Zero represents the ground state energy. Blue, red, and black bars show the ground state, S_1 state, and T_1 state, respectively. IRC path is connected by dashed lines.

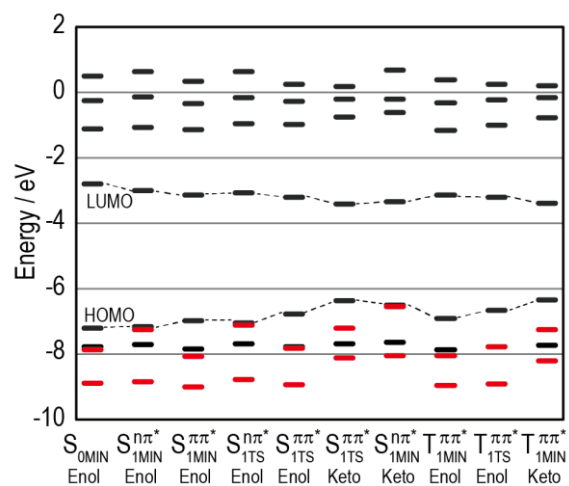


Figure S8. Orbital energies from HOMO-3 to LUMO+3 at each optimized structure of enol form (M06/cc-pVDZ). Black and red show π , π^* orbital and n orbital, respectively. HOMO and LUMO are connected by dashed lines.

Table S10. The emission energy, oscillator strength, and major transition at minimum structures obtained by geometry optimizations for enol form with various functionals and cc-pVDZ.

Functional	Minimum structure	Emission energy / eV	Oscillator strength	Major transitions	Contribution / %
M06	S ₁ MIN (enol, nπ*)	2.67	0.0005	HOMO-1 – LUMO	98.7
	S ₁ MIN (enol, ππ*)	2.95	0.0429	HOMO – LUMO	98.0
	S ₁ MIN (keto, nπ*)	1.69	0.0002	HOMO-1 – LUMO	99.2
	T ₁ MIN (enol, ππ*)	1.99		HOMO – LUMO	
	T ₁ MIN (keto, ππ*)	1.28		HOMO – LUMO	
B3LYP	S ₁ MIN (enol, nπ*)	2.53	0.0004	HOMO-1 – LUMO	99.4
	S ₁ MIN (enol, ππ*)	2.82	0.0393	HOMO – LUMO	98.0
	S ₁ MIN (keto, nπ*)	1.73	0.0002	HOMO-1 – LUMO	99.6
	S ₁ MIN (keto, ππ*)	2.12	0.0466	HOMO – LUMO	99.7
	T ₁ MIN (enol, ππ*)	2.00		HOMO – LUMO	
	T ₁ MIN (keto, ππ*)	1.29		HOMO – LUMO	
CAM-B3LYP	S ₁ MIN (enol, nπ*)	3.02	0.0007	HOMO-1 – LUMO	96.0
	S ₁ MIN (enol, ππ*)	3.27	0.0889	HOMO – LUMO	97.5
	S ₁ MIN (keto, nπ*)	2.13	0.0003	HOMO-1 – LUMO	97.1
	S ₁ MIN (keto, ππ*)	2.51	0.0890	HOMO – LUMO	99.4
	T ₁ MIN (enol, ππ*)	1.96		HOMO – LUMO	
	T ₁ MIN (keto, ππ*)	1.23		HOMO – LUMO	

Table S11. The emission energy, oscillator strength, and major transition at minimum structures obtained by geometry optimizations for lactam form dimer with M06/cc-pVDZ.

Functional	Minimum structure	Emission energy / eV	Oscillator strength	Major transitions	Contribution / %
M06	S _{1MIN} (lactam, n π^*)	2.60	0.0003	HOMO – LUMO	89.7
	T _{1MIN} (lactam, $\pi\pi^*$)	1.90		HOMO – LUMO	
	S _{1MIN} (enol, n π^*)	2.69	0.0005	HOMO – LUMO	89.0
	T _{1MIN} (enol, $\pi\pi^*$)	2.16		HOMO – LUMO	
	T _{1MIN} (enol, $\pi\pi^*$)	1.84		HOMO – LUMO	
	T _{1MIN} (isomer, n π^*)	0.83		HOMO – LUMO	

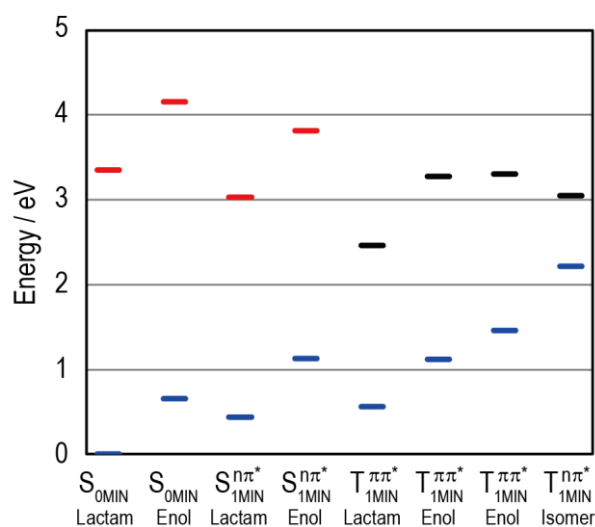


Figure S9. Relative energies of the ground and excited states of lactam form dimer at each optimized structure with M06/cc-pVDZ. Zero represents the ground state energy at **S**_{0MIN} of lactam form dimer. Blue, red and black bars show the ground state, S₁ state, and T₁ state, respectively.

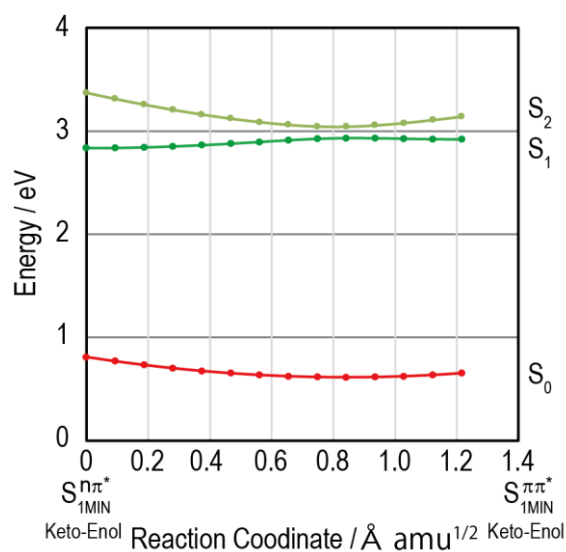


Figure S10. Potential energy curves along the linearly interpolated pathway which connects S_{1MIN} (keto-enol, $n\pi^*$) and S_{1MIN} (keto-enol, $\pi\pi^*$) of Zn-hqxc complex (M06/SDD (Zn), cc-pVDZ (other atoms)).

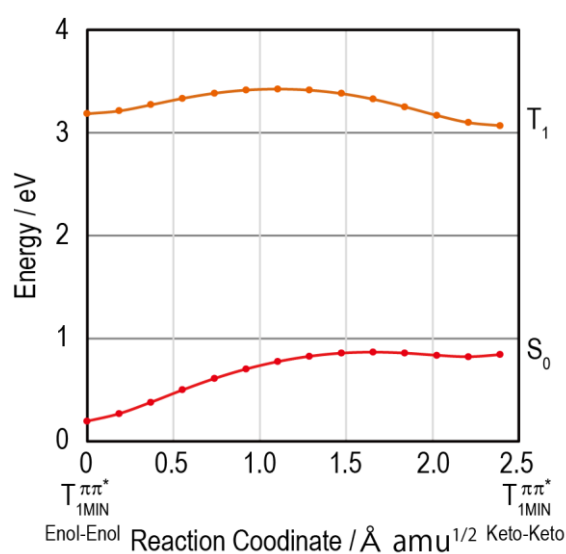


Figure S11. Potential energy curves along the linearly interpolated pathway which connects T_{1MIN} (enol-enol, $\pi\pi^*$) and T_{1MIN} (keto-keto, $\pi\pi^*$) of Zn-hqxc complex (M06/SDD (Zn), cc-pVDZ (other atoms)).

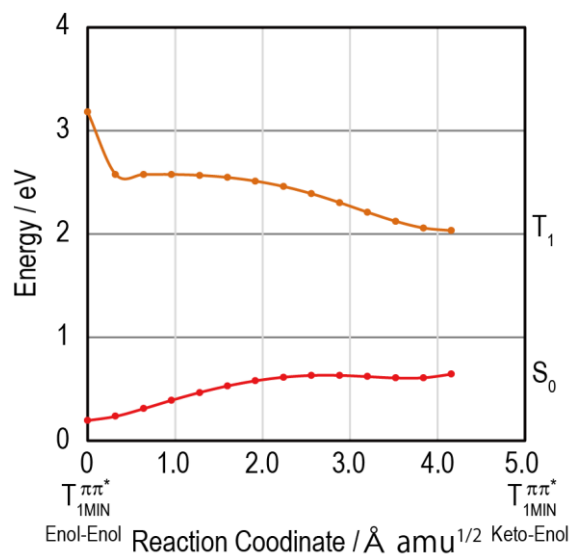


Figure S12. Potential energy curves along the linearly interpolated pathway which connects T_{1MIN} (enol-enol, $\pi\pi^*$) and T_{1MIN} (keto-enol, $\pi\pi^*$) of Zn-hqxc complex (M06/SDD (Zn), cc-pVDZ (other atoms)).

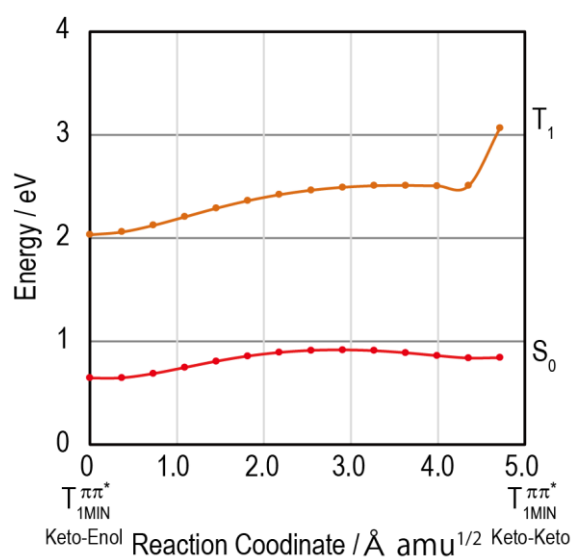


Figure S13. Potential energy curves along the linearly interpolated pathway which connects T_{1MIN} (keto-enol, $\pi\pi^*$) and T_{1MIN} (keto-keto, $\pi\pi^*$) of Zn-hqxc complex (M06/SDD (Zn), cc-pVDZ (other atoms)).

Table S12. The emission energy, oscillator strength, and major transition at minimum structures obtained by geometry optimizations for Zn-hqxc complex with various functionals and SDD (Zn) and cc-pVDZ (other atoms).

Functional	Minimum structure	Emission energy / eV	Oscillator strength	Major transitions	Contribution / %
M06	S _{1MIN} (keto-enol, $n\pi^*$)	2.03	0.0006	HOMO-1 – LUMO	93.9
	S _{1MIN} (keto-enol, $\pi\pi^*$)	2.27	0.0752	HOMO – LUMO	94.7
	T _{1MIN} (enol-enol, $\pi\pi^*$)	2.99		HOMO – LUMO	
	T _{1MIN} (keto-enol, $\pi\pi^*$)	1.39		HOMO – LUMO	
	T _{1MIN} (keto-keto, $\pi\pi^*$)	2.23		HOMO – LUMO	
B3LYP	S _{1MIN} (keto-enol, $n\pi^*$)	2.06	0.0007	HOMO-1 – LUMO	96.5
	S _{1MIN} (keto-enol, $\pi\pi^*$)	2.17	0.0689	HOMO – LUMO	99.3
	T _{1MIN} (enol-enol, $\pi\pi^*$)	2.78		HOMO – LUMO	
	T _{1MIN} (keto-enol, $\pi\pi^*$)	1.40		HOMO – LUMO	
	T _{1MIN} (keto-keto, $\pi\pi^*$)	2.13		HOMO – LUMO	
CAM-B3LYP	S _{1MIN} (keto-enol, $\pi\pi^*$)	2.59	0.1213	HOMO – LUMO	98.8
	T _{1MIN} (keto-enol, $\pi\pi^*$)	1.35		HOMO – LUMO	
BHandHLYP	S _{1MIN} (keto-enol, $\pi\pi^*$)	2.70	0.1392	HOMO – LUMO	99.1
	T _{1MIN} (enol-enol, $\pi\pi^*$)	3.61		HOMO – LUMO	
	T _{1MIN} (keto-enol, $\pi\pi^*$)	1.17		HOMO – LUMO	
	T _{1MIN} (keto-keto, $\pi\pi^*$)	2.72		HOMO – LUMO	

Table S13. Coordinates of lactam form dimer at S_{0MIN} (M06/cc-pVDZ).

Atom	Coordinates (Å)		
	x	y	z
O	-0.747571	-1.600977	0.002319
O	-2.196086	-3.800078	0.001722
O	-4.410040	-3.593249	0.000910
N	-1.810463	0.400628	0.000874
N	-4.246283	-0.876547	-0.000435
C	-3.323378	-3.088498	0.001059
C	-3.153699	-1.574998	0.000534
C	-1.818015	-0.955328	0.001277
C	-2.950378	1.169086	-0.000254
C	-2.900414	2.567837	-0.000714
C	-4.088290	3.276840	-0.001749
C	-5.330955	2.616790	-0.002324
C	-5.379624	1.238364	-0.001890
C	-4.187291	0.489371	-0.000859
H	-1.930689	3.072660	-0.000257
H	-4.057477	4.368850	-0.002091
H	-6.253637	3.200411	-0.003124
H	-6.320005	0.683062	-0.002305
H	-0.879253	0.862084	0.001104
H	-1.427290	-3.186210	0.002431
O	0.747740	1.601421	0.001141
O	2.196940	3.800530	0.002332

O	4.410788	3.592870	0.000207
N	1.810248	-0.400412	-0.000096
N	4.246326	0.876345	0.000101
C	3.323953	3.088478	0.001091
C	3.153887	1.575025	0.000705
C	1.818080	0.955590	0.000617
C	2.950041	-1.169037	-0.000713
C	2.899848	-2.567811	-0.001479
C	4.087656	-3.276984	-0.002078
C	5.330380	-2.617158	-0.001917
C	5.379311	-1.238733	-0.001165
C	4.187089	-0.489563	-0.000576
H	1.930025	-3.072431	-0.001578
H	4.056551	-4.368992	-0.002680
H	6.252999	-3.200903	-0.002393
H	6.319786	-0.683615	-0.000997
H	0.878988	-0.861830	0.000152
H	1.427828	3.187057	0.002199

Table S14. Coordinates of lactam form monomer at $S_{0\text{MIN}}$ (M06/cc-pVDZ).

Atom	Coordinates (Å)		
	x	y	z
O	-1.927620	2.070065	-0.000039
O	-3.635524	0.069694	-0.000827
O	-2.827534	-2.002518	0.000840
N	0.286931	1.607410	0.000327
N	-0.259023	-1.087568	-0.000057
C	-2.644089	-0.817616	0.000075
C	-1.234426	-0.238434	0.000022
C	-1.031141	1.227949	0.000070
C	1.349795	0.731649	0.000156
C	2.679891	1.162387	0.000207
C	3.692836	0.217336	-0.000021
C	3.403419	-1.156189	-0.000277
C	2.089027	-1.581054	-0.000291
C	1.039970	-0.644976	-0.000074
H	2.905320	2.232562	0.000407
H	4.733302	0.550731	0.000000
H	4.216954	-1.883974	-0.000460
H	1.814391	-2.638135	-0.000466
H	0.449671	2.612929	0.000381
H	-3.261255	0.982754	-0.000745

Table S15. Coordinates of enol form at S_{0MIN} with M06/cc-pVDZ.

Atom	Coordinates (Å)		
	x	y	z
O	-1.909149	2.136731	0.000025
O	-3.571899	0.073266	-0.000177
O	-2.721944	-1.985797	0.000061
N	0.305002	1.692069	0.000030
N	-0.254870	-1.066553	-0.000030
C	-2.608355	-0.669205	-0.000127
C	-1.206650	-0.161774	-0.000031
C	-0.928605	1.248864	0.000005
C	1.296095	0.770041	0.000031
C	2.646216	1.198567	0.000065
C	3.662894	0.275323	0.000067
C	3.390093	-1.115626	0.000037
C	2.094022	-1.564466	0.000007
C	1.027259	-0.633035	0.000004
H	2.833271	2.274469	0.000087
H	4.701776	0.614729	0.000091
H	4.218139	-1.827764	0.000039
H	1.845696	-2.628526	-0.000017
H	-1.803334	-2.332104	0.000163
H	-2.760341	1.634857	0.000033

Table S16. Coordinates of Zn-hqxc complex at $S_{0\text{MIN}}$ (M06/SDD (Zn), cc-pVDZ (other atoms)).

Atom	Coordinates (Å)		
	x	y	z
Zn	0.000000	0.000000	0.00000
S	2.240987	-0.650300	2.143328
O	0.692677	-1.925348	-0.045554
(O	1.949999	-3.334191	-1.248902
O	3.441018	-2.431979	-3.127859
O	1.139716	0.374275	1.751460
N	1.721065	0.179310	-1.374268
N	3.538600	-0.202307	-3.475218
C	2.237956	1.256921	-2.025617
C	1.878382	2.569812	-1.638756
C	2.399639	3.640813	-2.325189
C	3.288095	3.435955	-3.407868
C	3.656762	2.168202	-3.789648
C	3.147776	1.039616	-3.101124
C	3.053305	-1.216323	-2.798575
C	2.105963	-1.024639	-1.725604
C	1.535671	-2.202875	-0.957977
C	3.002743	0.167094	3.565359
C	1.370290	-1.953295	3.050878
H	1.181557	2.693177	-0.803336
H	2.129547	4.658225	-2.032321
H	3.690631	4.300599	-3.942223

H	4.349288	1.983858	-4.614018
H	3.515032	1.059260	3.181775
H	2.199651	0.460415	4.257195
H	3.722795	-0.513810	4.041842
H	0.821088	-2.530349	2.293718
H	0.679336	-1.472006	3.760575
H	2.107847	-2.587563	3.564528
H	2.966675	-3.049166	-2.495083
S	-2.240987	0.650300	-2.143328
O	-0.692677	1.925348	0.045554
O	-1.949999	3.334191	1.248902
O	-3.441018	2.431979	3.127859
O	-1.139716	-0.374275	-1.751460
N	-1.721065	-0.179310	1.374268
N	-3.538600	0.202307	3.475218
C	-2.237956	-1.256921	2.025617
C	-1.878382	-2.569812	1.638756
C	-2.399639	-3.640813	2.325189
C	-3.288095	-3.435955	3.407868
C	-3.656762	-2.168202	3.789648
C	-3.147776	-1.039616	3.101124
C	-3.053305	1.216323	2.798575
C	-2.105963	1.024639	1.725604
C	-1.535671	2.202875	0.957977
C	-3.002743	-0.167094	-3.565359

C	-1.370290	1.953295	-3.050878
H	-1.181557	-2.693177	0.803336
H	-2.129547	-4.658225	2.032321
H	-3.690631	-4.300599	3.942223
H	-4.349288	-1.983858	4.614018
H	-3.515032	-1.059260	-3.181775
H	-2.199651	-0.460415	-4.257195
H	-3.722795	0.513810	-4.041842
H	-0.821088	2.530349	-2.293718
H	-0.679336	1.472006	-3.760575
H	-2.107847	2.587563	-3.564528
H	-2.966675	3.049166	2.495083

REFERENCES

- (1) Wu, J.; Liu, W.; Ge, J.; Zhang, H.; Wang, P. New Sensing Mechanisms for Design of Fluorescent Chemosensors Emerging in Recent Years. *Chem. Soc. Rev.* **2011**, *40* (7), 3483–3495.
- (2) Liu, Z.; He, W.; Guo, Z. Metal Coordination in Photoluminescent Sensing. *Chem. Soc. Rev.* **2013**, *42* (4), 1568–1600.
- (3) Tian, D.; Qi, F.; Ma, H.; Wang, X.; Pan, Y.; Chen, R.; Shen, Z.; Liu, Z.; Huang, L.; Huang, W. Domino-like Multi-Emissions across Red and near Infrared from Solid-State 2-/2,6-Aryl Substituted BODIPY Dyes. *Nat. Commun.* **2018**, *9* (1), 2688–2696.
- (4) Eber, G.; Grüneis, S.; Schneider, S.; Dörr, F. Dual Fluorescence Emission of Azulene Derivatives in Solution. *Chem. Phys Lett.* **1974**, *29*, 397–404.
- (5) Samanta, S.; Roy, M. B.; Chatterjee, M.; Ghosh, S. Simultaneous Emissions from T₂ and T₁ States of Naphthalene Moiety in a Specially Designed Naphthalene Cryptand. *J. Lumin.* **2007**, *126* (1), 230–238.

- (6) Han, J.; Loudet, A.; Barhoumi, R.; Burghardt, R. C.; Burgess, K. A Ratiometric PH Reporter for Imaging Protein-Dye Conjugates in Living Cells. *J. Am. Chem. Soc.* **2009**, *131* (5), 1642–1643.
- (7) Gale, P. A.; Caltagirone, C. Anion Sensing by Small Molecules and Molecular Ensembles. *Chem. Soc. Rev.* **2015**, *44* (13), 4212–4227.
- (8) Zhou, C.; Zhang, S.; Gao, Y.; Liu, H.; Shan, T.; Liang, X.; Yang, B.; Ma, Y. Ternary Emission of Fluorescence and Dual Phosphorescence at Room Temperature: A Single-Molecule White Light Emitter Based on Pure Organic Aza-Aromatic Material. *Adv. Funct. Mater.* **2018**, *28* (32), 1802407–1802412.
- (9) Kwon, J. E.; Park, S. Y. Advanced Organic Optoelectronic Materials: Harnessing Excited-State Intramolecular Proton Transfer (ESIPT) Process. *Adv. Mater.* **2011**, *23* (32), 3615–3642.
- (10) Zhao, J.; Ji, S.; Chen, Y.; Guo, H.; Yang, P. Excited State Intramolecular Proton Transfer (ESIPT): From Principal Photophysics to the Development of New Chromophores and Applications in Fluorescent Molecular Probes and Luminescent Materials. *Phys. Chem. Chem. Phys.* **2012**, *14* (25), 8803–8817.
- (11) Tomin, V. I.; Demchenko, A. P.; Chou, P. T. Thermodynamic vs. Kinetic Control of Excited-State Proton Transfer Reactions. *J. Photochem. Photobiol. C Photochem. Rev.* **2015**, *22*, 1–18.
- (12) Padalkar, V. S.; Sakamaki, D.; Tohnai, N.; Akutagawa, T.; Sakai, K.-I.; Seki, S. Highly Emissive Excited-State Intramolecular Proton Transfer (ESIPT) Inspired 2-(2'-Hydroxy)Benzothiazole–fluorene Motifs: Spectroscopic and Photophysical Properties Investigation. *RSC Adv.* **2015**, *5* (98), 80283–80296.
- (13) Stasyuk, A. J.; Cywiński, P. J.; Gryko, D. T. Excited-State Intramolecular Proton Transfer in 2'-(2'-Hydroxyphenyl)Imidazo[1,2-*a*]Pyridines. *J. Photochem. Photobiol. C Photochem. Rev.* **2016**, *28*, 116–137.
- (14) Padalkar, V. S.; Seki, S. Excited-State Intramolecular Proton-Transfer (ESIPT)-Inspired Solid State Emitters. *Chem. Soc. Rev.* **2016**, *45* (1), 169–202.
- (15) Yao, D.; Zhao, S.; Guo, J.; Zhang, Z.; Zhang, H.; Liu, Y.; Wang, Y. Hydroxyphenyl-Benzothiazole Based Full Color Organic Emitting Materials Generated by Facile Molecular Modification. *J. Mater. Chem.* **2011**, *21* (11), 3568–3570.
- (16) Sakai, K.-I.; Kawamura, H.; Kobayashi, N.; Ishikawa, T.; Ikeda, C.; Kikuchi, T.; Akutagawa, T. Highly Efficient Solid-State Red Fluorophores Using ESIPT: Crystal Packing and Fluorescence Properties of

- Alkoxy-Substituted Dibenzothiazolylphenols. *CrystEngComm* **2014**, *16* (15), 3180–3185.
- (17) Park, S.; Ji, E. K.; Se, H. K.; Seo, J.; Chung, K.; Park, S. Y.; Jang, D. J.; Medina, B. M.; Gierschner, J.; Soo, Y. P. A White-Light-Emitting Molecule: Frustrated Energy Transfer between Constituent Emitting Centers. *J. Am. Chem. Soc.* **2009**, *131* (39), 14043–14049.
- (18) Tang, K.-C.; Chang, M.-J.; Lin, T.-Y.; Pan, H.-A.; Fang, T.-C.; Chen, K.-Y.; Hung, W.-Y.; Hsu, Y.-H.; Chou, P.-T. Fine Tuning the Energetics of Excited-State Intramolecular Proton Transfer (ESIPT): White Light Generation in A Single ESIPT System. *J. Am. Chem. Soc.* **2011**, *133* (44), 17738–17745.
- (19) Benelhadj, K.; Muzuzu, W.; Massue, J.; Retailleau, P.; Charaf-Eddin, A.; Laurent, A. D.; Jacquemin, D.; Ulrich, G.; Ziessel, R. White Emitters by Tuning the Excited-State Intramolecular Proton-Transfer Fluorescence Emission in 2-(2-Hydroxybenzofuran)Benzoxazole Dyes. *Chem. - A Eur. J.* **2014**, *20* (40), 12843–12857.
- (20) Sakai, K.-I.; Tsuchiya, S.; Kikuchi, T.; Akutagawa, T. An ESIPT Fluorophore with a Switchable Intramolecular Hydrogen Bond for Applications in Solid-State Fluorochromism and White Light Generation. *J. Mater. Chem. C* **2016**, *4* (10), 2011–2016.
- (21) Heyer, E.; Benelhadj, K.; Budzák, S.; Jacquemin, D.; Massue, J.; Ulrich, G. On the Fine-Tuning of the Excited-State Intramolecular Proton Transfer (ESIPT) Process in 2-(2'-Hydroxybenzofuran)Benzazole (HBBX) Dyes. *Chem. - A Eur. J.* **2017**, *23* (30), 7324–7336.
- (22) Serdiuk, I. E. Design and Emissive Features of Ionic White-Light Fluorophore. *J. Phys. Chem. C* **2018**, *122* (32), 18615–18620.
- (23) Mutai, T.; Tomoda, H.; Ohkawa, T.; Yabe, Y.; Araki, K. Switching of Polymorph-Dependent ESIPT Luminescence of an Imidazo[1,2-*a*]Pyridine Derivative. *Angew. Chem. Int. Ed.* **2008**, *47* (49), 9522–9524.
- (24) Tang, B.; Zhang, H.; Ye, K.; Zhang, H.; Wang, Y. Highly Efficient Blue Solid Emitters and Tautomerization-Induced ON/OFF Fluorescence Switching Based on Structurally Simple 3(5)-Phenol-1H -Pyrazoles. *Chem. Commun.* **2016**, *52* (89), 13128–13131.
- (25) Nayak, M. K.; Dogra, S. K. Excited State Prototropism in 2-Aminonicotinic Acid: Effect of Solvents and Acid-Base Concentrations. *J. Photochem. Photobiol. A Chem.* **2005**, *171* (3), 281–290.

- (26) Shaikh, M.; Choudhury, S. D.; Mohanty, J.; Bhasikuttan, A. C.; Nau, W. M.; Pal, H. Modulation of Excited-State Proton Transfer of 2-(2'-Hydroxyphenyl)Benzimidazole in a Macrocyclic Cucurbit[7]Uril Host Cavity: Dual Emission Behavior and pK_a Shift. *Chem. Eur. J.* **2009**, *15* (45), 12362–12370.
- (27) Ciuciu, A. I.; Skonieczny, K.; Koszelewski, D.; Gryko, D. T.; Flamigni, L. Dynamics of Intramolecular Excited State Proton Transfer in Emission Tunable, Highly Luminescent Imidazole Derivatives. *J. Phys. Chem. C* **2013**, *117* (2), 791–803.
- (28) Suzuki, N.; Fukazawa, A.; Nagura, K.; Saito, S.; Kitoh-Nishioka, H.; Yokogawa, D.; Irle, S.; Yamaguchi, S. A Strap Strategy for Construction of an Excited-State Intramolecular Proton Transfer (ESIPT) System with Dual Fluorescence. *Angew. Chem. Int. Ed.* **2014**, *53* (31), 8231–8235.
- (29) Tong, S.; Zhao, S.; He, Q.; Wang, Q.; Wang, M.; Zhu, J. Fluorophores for Excited-State Intramolecular Proton Transfer by an Yttrium Triflate Catalyzed Reaction of Isocyanides with Thiocarboxylic Acids. *Angew. Chem. Int. Ed.* **2017**, *56*, 6599–6603.
- (30) Vázquez, S. R.; Rodríguez, M. C. R.; Mosquera, M.; Rodríguez-Prieto, F. Rotamerism, Tautomerism, and Excited-State Intramolecular Proton Transfer in 2-(4'-*N,N*-Diethylamino-2'-Hydroxyphenyl)Benzimidazoles: Novel Benzimidazoles Undergoing Excited-State Intramolecular Coupled Proton and Charge Transfer. *J. Phys. Chem. A* **2008**, *112* (3), 376–387.
- (31) Peng, C. Y.; Shen, J. Y.; Chen, Y. T.; Wu, P. J.; Hung, W. Y.; Hu, W. P.; Chou, P. T. Optically Triggered Stepwise Double-Proton Transfer in an Intramolecular Proton Relay: A Case Study of 1,8-Dihydroxy-2-Naphthaldehyde. *J. Am. Chem. Soc.* **2015**, *137* (45), 14349–14357.
- (32) Qinghui, C.; Medvetz, D. A.; Yi, P. A Polymeric Colorimetric Sensor with Excited-State Intramolecular Proton Transfer for Anionic Species. *Chem. Mater.* **2007**, *19* (26), 6421–6429.
- (33) Sahoo, S. K.; Bera, R. K.; Baral, M.; Kanungo, B. K. Excited State Intramolecular Proton Transfer (ESIPT) in a Dioxotetraamine Derived Schiff Base and Its Complexation with Fe(III) and Cr(III). *J. Photochem. Photobiol. A Chem.* **2007**, *188* (2–3), 298–310.
- (34) Wang, J.; Chu, Q.; Liu, X.; Wesdemiotis, C.; Pang, Y. Large Fluorescence Response by Alcohol from a Bis(Benzoxazole)-Zinc(II) Complex: The Role of Excited State Intramolecular Proton Transfer. *J. Phys.*

Chem. B **2013**, *117* (15), 4127–4133.

- (35) Nakane, Y.; Takeda, T.; Hoshino, N.; Sakai, K.-I.; Akutagawa, T. Cation–Anion Dual Sensing of a Fluorescent Quinoxalinone Derivative Using Lactam–Lactim Tautomerism. *J. Phys. Chem. A* **2015**, *119* (24), 6223–6231.
- (36) Ali, R.; Razi, S. S.; Srivastava, P.; Shahid, M.; Misra, A. A Polynuclear Hetero Atom Containing Molecular Organic Scaffold to Detect Al^{3+} Ion through a Fluorescence Turn-on Response. *RSC Adv.* **2015**, *5* (76), 61513–61520.
- (37) Alam, R.; Mistri, T.; Bhowmick, R.; Katarkar, A.; Chaudhuri, K.; Ali, M. ESIPT Blocked CHEF Based Differential Dual Sensor for Zn^{2+} and Al^{3+} in a Pseudo-Aqueous Medium with Intracellular Bio-Imaging Applications and Computational Studies. *RSC Adv.* **2016**, *6* (2), 1268–1278.
- (38) Jagadesan, P.; Whittemore, T.; Beirl, T.; Turro, C.; McGrier, P. L. Excited-State Intramolecular Proton-Transfer Properties of Three Tris(N-Salicylideneaniline)-Based Chromophores with Extended Conjugation. *Chem. - A Eur. J.* **2017**, *23* (4), 917–925.
- (39) Tsuchiya, S.; Sakai, K.-I.; Kawano, K.; Nakane, Y.; Kikuchi, T.; Akutagawa, T. Color Changes of a Full-Color Emissive ESIPT Fluorophore in Response to Recognition of Certain Acids and Their Conjugate Base Anions. *Chem. Eur. J.* **2018**, *24*, 1–9.
- (40) Dixit, M. K.; Dubey, M. Li^+ -Induced Fluorescent Metallogel: A Case of ESIPT-CHEF and ICT Phenomenon. *Phys. Chem. Chem. Phys.* **2018**, *20* (36), 23762–23772.
- (41) Chudoba, C.; Riedle, E.; Pfeiffer, M.; Elsaesser, T. Vibrational Coherence in Ultrafast Excited State Proton Transfer. *Chem. Phys. Lett.* **1996**, *263* (5), 622–628.
- (42) Lochbrunner, S.; Wurzer, A. J.; Riedle, E. Ultrafast Excited-State Proton Transfer and Subsequent Coherent Skeletal Motion of 2-(2'-Hydroxyphenyl)Benzothiazole. *J. Chem. Phys.* **2000**, *112* (24), 10699–10702.
- (43) Barbatti, M.; Aquino, A. J.; Lischka, H.; Schrieffer, C.; Lochbrunner, S.; Riedle, E. Ultrafast Internal Conversion Pathway and Mechanism in 2-(2'-Hydroxyphenyl)Benzothiazole: A Case Study for Excited-State Intramolecular Proton Transfer Systems. *Phys. Chem. Chem. Phys.* **2009**, *11*, 1406–1415.
- (44) Dick, B.; Ernsting, N. P. Excited-State Intramolecular Proton Transfer in 3-Hydroxyflavone Isolated in

- Solid Argon: Fluorescence and Fluorescence-Excitation Spectra and Tautomer Fluorescence Rise Time. *J. Phys. Chem.* **1987**, *91* (16), 4261–4265.
- (45) Elsaesser, T.; Kaiser, W. Visible and Infrared Spectroscopy of Intramolecular Proton Transfer Using Picosecond Laser Pulses. *Chem. Phys. Lett.* **1986**, *128* (3), 231–237.
- (46) Chou, P. T.; Yu, W. S.; Cheng, Y. M.; Pu, S. C.; Yu, Y. C.; Lin, Y. C.; Huang, C. H.; Chen, C. T. Solvent-Polarity Tuning Excited-State Charge Coupled Proton-Transfer Reaction in *p*-*N,N*-Ditolylaminosalicylaldehydes. *J. Phys. Chem. A* **2004**, *108* (31), 6487–6498.
- (47) Yin, H.; Li, H.; Xia, G.; Ruan, C.; Shi, Y.; Wang, H.; Jin, M.; Ding, D. A Novel Non-Fluorescent Excited State Intramolecular Proton Transfer Phenomenon Induced by Intramolecular Hydrogen Bonds: An Experimental and Theoretical Investigation. *Sci. Rep.* **2016**, *6*, 19774–19782.
- (48) Shigemitsu, Y.; Mutai, T.; Houjou, H.; Araki, K. Excited-State Intramolecular Proton Transfer (ESIPT) Emission of Hydroxyphenylimidazopyridine: Computational Study on Enhanced and Polymorph-Dependent Luminescence in the Solid State. *J. Phys. Chem. A* **2012**, *116*, 12041–12048.
- (49) Cui, Y.; Zhao, H.; Jiang, L.; Li, P.; Ding, Y.; Song, P.; Xia, L. Solvation Effect on the Excited-State Intramolecular Proton Transfer Mechanism of 1-Morpholinylmethyl-2-Naphthol. *Comput. Theor. Chem.* **2015**, *1074*, 125–130.
- (50) Tsai, H.-H. G.; Sun, H.-L. S.; Tan, C.-J. TD-DFT Study of the Excited-State Potential Energy Surfaces of 2-(2'-Hydroxyphenyl)Benzimidazole and Its Amino Derivatives. *J. Phys. Chem. A* **2010**, *114* (12), 4065–4079.
- (51) Nishina, N.; Mutai, T.; Aihara, J. Excited-State Intramolecular Proton Transfer and Global Aromaticity. *J. Phys. Chem. A* **2017**, *121* (1), 151–161.
- (52) Scheiner, S. Theoretical Studies of Excited State Proton Transfer in Small Model Systems. *J. Phys. Chem. A* **2000**, *104* (25), 5898–5909.
- (53) Guan, P. J.; Cui, G.; Fang, Q. Computational Photochemistry of the Azobenzene Scaffold of Sudan I and Orange II Dyes: Excited-State Proton Transfer and Deactivation via Conical Intersections. *ChemPhysChem* **2015**, *16* (4), 805–811.

- (54) Yang, W.; Chen, X. Dual Fluorescence of Excited State Intra-Molecular Proton Transfer of HBFO: Mechanistic Understanding, Substituent and Solvent Effects. *Phys. Chem. Chem. Phys.* **2014**, *16* (9), 4242–4250.
- (55) Azarias, C.; Budzák, Š.; Laurent, A. D.; Ulrich, G.; Jacquemin, D. Tuning ESIPT Fluorophores into Dual Emitters. *Chem. Sci.* **2016**, *7* (6), 3763–3774.
- (56) Chi, Y.; Chou, P. T. Transition-Metal Phosphors with Cyclometalating Ligands: Fundamentals and Applications. *Chem. Soc. Rev.* **2010**, *39* (2), 638–655.
- (57) Baggaley, E.; Weinstein, J. A.; Williams, J. A. G. Lighting the Way to See inside the Live Cell with Luminescent Transition Metal Complexes. *Coord. Chem. Rev.* **2012**, *256* (15–16), 1762–1785.
- (58) Wenger, O. S. Vapochromism in Organometallic and Coordination Complexes: Chemical Sensors for Volatile Organic Compounds. *Chem. Rev.* **2013**, *113* (5), 3686–3733.
- (59) Fan, C.; Yang, C. Yellow/Orange Emissive Heavy-Metal Complexes as Phosphors in Monochromatic and White Organic Light-Emitting Devices. *Chem. Soc. Rev.* **2014**, *43* (17), 6439–6469.
- (60) Cariati, E.; Lucenti, E.; Botta, C.; Giovanella, U.; Marinotto, D.; Righetto, S. Cu(I) Hybrid Inorganic-Organic Materials with Intriguing Stimuli Responsive and Optoelectronic Properties. *Coord. Chem. Rev.* **2016**, *306*, 566–614.
- (61) Kayanuma, M.; Daniel, C.; Köppel, H.; Gindensperger, E. Photophysics of Isomerizable Re(I) Complexes: A Theoretical Analysis. *Coord. Chem. Rev.* **2011**, *255* (21–22), 2693–2703.
- (62) Baková, R.; Chergui, M.; Daniel, C.; Vlček Jr., A.; Zális, S. Relativistic Effects in Spectroscopy and Photophysics of Heavy-Metal Complexes Illustrated by Spin–orbit Calculations of $[\text{Re}(\text{Imidazole})(\text{CO})_3(\text{Phen})]^+$. *Coord. Chem. Rev.* **2011**, *255* (7–8), 975–989.
- (63) Kamiya, M.; Taketsugu, T. Ab Initio Surface Hopping Excited-State Molecular Dynamics Approach on the Basis of Spin – Orbit Coupled States : An Application to the A-Band Photodissociation of CH_3I . *J. Comput. Chem.* **2019**, *40* (2), 456–463.
- (64) Harabuchi, Y.; Eng, J.; Gindensperger, E.; Taketsugu, T.; Maeda, S.; Daniel, C. Exploring the Mechanism of Ultrafast Intersystem Crossing in Rhenium(I) Carbonyl Bipyridine Halide Complexes: Key Vibrational

- Modes and Spin-Vibronic Quantum Dynamics. *J. Chem. Theory Comput.* **2016**, *12* (5), 2335–2345.
- (65) Penfold, T. J.; Gindensperger, E.; Daniel, C.; Marian, C. M. Spin-Vibronic Mechanism for Intersystem Crossing. *Chem. Rev.* **2018**, *118* (15), 6975–7025.
- (66) Nah, M. K.; Rho, S. G.; Kim, H. K.; Kang, J. G. Sensitized Near-IR Luminescence of Ln(III) Complexes with Benzothiazole Derivatives. *J. Phys. Chem. A* **2007**, *111* (45), 11437–11443.
- (67) Małecki, J. G.; Maron, A.; Kusz, J. Phosphorescence of a Ruthenium (II) Hydride-Carbonyl Complex with 3-Hydroxy-2-Quinoxalinecarboxylic Acid as a Co-Ligand. *Mendeleev Commun.* **2015**, *25*, 103–105.
- (68) Chen, L.; Yan, C.; Pan, M.; Wang, H. P.; Fan, Y. N.; Su, C. Y. Multi-Mode White Light Emission in a Zn^{II} Coordination Polymer from Excited-State Intramolecular Proton Transfer (ESIPT) Ligands. *Eur. J. Inorg. Chem.* **2016**, *17*, 2676–2680.
- (69) Chen, L.; Ye, J. W.; Wang, H. P.; Pan, M.; Yin, S. Y.; Wei, Z. W.; Zhang, L. Y.; Wu, K.; Fan, Y. N.; Su, C. Y. Ultrafast Water Sensing and Thermal Imaging by a Metal-Organic Framework with Switchable Luminescence. *Nat. Commun.* **2017**, *8*, 15985–15995.
- (70) Sun, S.-S.; Zhang, J.-H.; Wang, Z.; Yu, Y.-Q.; Zhu, C.-Y.; Pan, M.; Su, C.-Y. Anomalous Thermally-Activated NIR Emission of ESIPT Modulated Nd-Complexes for Optical Fiber Sensing Devices. *Chem. Commun.* **2018**, *54* (49), 6304–6307.
- (71) Sun, S.-S.; Wang, Z.; Wu, X. W.; Zhang, J.-H.; Li, C.-J.; Yin, S.-Y.; Chen, L.; Pan, M.; Su, C.-Y. ESIPT-Modulated Emission of Lanthanide Complexes: Different Energy-Transfer Pathways and Multiple Responses. *Chem. Eur. J.* **2018**, *24* (40), 10091–10098.
- (72) Sakai, K.-I.; Takahashi, S.; Kobayashi, A.; Akutagawa, T.; Nakamura, T.; Dosen, M.; Kato, M.; Nagashima, U. Excited State Intramolecular Proton Transfer (ESIPT) in Six-Coordinated Zinc(II)-Quinoxaline Complexes with Ligand Hydrogen Bonds: Their Fluorescent Properties Sensitive to Axial Positions. *Dalt. Trans.* **2010**, *39* (8), 1989–1995.
- (73) Badoğlu, S.; Yurdakul, Ş. A Study of the Molecular Structure and Spectroscopic Properties of 3-Hydroxy-2-Quinoxalinecarboxylic Acid by Experimental Methods and Quantum Chemical Calculations. *Spectrochim. Acta Part A Mol. Biomol. Spectrosc.* **2013**, *101*, 14–21.

- (74) Badoğlu, S.; Yurdakul, Ş. DFT Study of Solvent Effects on 3-Hydroxy-2-Quinoxalinecarboxylic Acid Tautomers. *Opt. Spectrosc.* **2014**, *117* (2), 201–212.
- (75) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenb, D. J. Gaussian09. Gaussian Inc.; Wallingfold, CT 2009.
- (76) Gonzalez, C.; Bernhard Schlegel, H. An Improved Algorithm for Reaction Path Following. *J. Chem. Phys.* **1989**, *90* (4), 2154–2161.
- (77) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Petersson, G. A.; Nakatsuji, H.; Li, X.; Caricato, M.; Marenich, A. V.; Bloino, J.; Janesko, B. G.; Gomperts, R.; Mennucci, B.; Hratch, D. J. Gaussian16. Gaussian Inc.; Wallingfold, CT 2016.
- (78) Zhao, Y.; Truhlar, D. G. The M06 Suite of Density Functionals for Main Group Thermochemistry, Thermochemical Kinetics, Noncovalent Interactions, Excited States, and Transition Elements: Two New Functionals and Systematic Testing of Four M06-Class Functionals and 12 Other Function. *Theor. Chem. Acc.* **2008**, *120* (1–3), 215–241.
- (79) Dunning Jr., T. H.; Hay, P. J. In: *Modern Theoretical Chemistry, Plenum, New York*; 1976, 1-28.
- (80) Dunning Jr., T. H. Gaussian Basis Sets for Use in Correlated Molecular Calculations. III. The Atoms Aluminum through Argon. *J. Chem. Phys.* **1989**, *90* (2), 1007–1023.
- (81) Becke, A. D. Density-Functional Exchange-Energy Approximation with Correct Asymptotic Behavior. *Phys. Rev. A* **1988**, *38* (6), 3098–3100.
- (82) Lee, C.; Yang, W.; Parr, R. G. Development of the Colle-Salvetti Correlation-Energy Formula into a Functional of the Electron Density. *Phys. Rev. B* **1988**, *37* (2), 785–789.
- (83) Becke, A. D. Density-Functional Thermochemistry.III. The Role of Exact Exchange. *J. Chem. Phys.* **1993**, *98* (7), 5648–5652.
- (84) Yanai, T.; Tew, D. P.; Handy, N. C. A New Hybrid Exchange – Correlation Functional Using the Coulomb-Attenuating Method (CAM-B3LYP). *Chem. Phys. Lett.* **2004**, *393* (1–3), 51–57.
- (85) Becke, A. D. A New Mixing of Hartree-Fock and Local Density-Functional Theories. *J. Chem. Phys.* **1993**,

98 (2), 1372–1377.

- (86) Christiansen, O.; Koch, H.; Jørgensen, P. The Second-Order Approximate Coupled Cluster Singles and Doubles Model CC2. *Chem. Phys. Lett.* **1995**, *243* (5–6), 409–418.
- (87) Schäfer, A.; Horn, H.; Ahlrichs, R. Fully Optimized Contracted Gaussian Basis Sets for Atoms Li to Kr. *J. Chem. Phys.* **1992**, *97* (4), 2571–2577.
- (88) Ahlrichs, R.; Bär, M.; Marco, H.; Horn, H.; Kölmel, C. ELECTRONIC STRUCTURE CALCULATIONS ON WORKSTATION COMPUTERS: THE PROGRAM SYSTEM TURBOMOLE. *Chem. Phys. Lett.* **1989**, *162* (3), 165–169.
- (89) Dapprich, S.; Komáromi, I.; Byun, K. S.; Morokuma, K. A New ONIOM Implementation in Gaussian98 . Part I . The Calculation of Energies , Gradients , Vibrational Frequencies and Electric Field Derivatives. *J. Mol. Struct.* **1999**, *461–462*, 1–21.
- (90) Rappé, A. K.; Casewit, C. J.; Colwell, K. S.; Goddard III, W. A.; Skiff, W. M. UFF, a Full Periodic Table Force Field for Molecular Mechanics and Molecular Dynamics Simulations. *J. Am. Chem. Soc.* **1992**, *114* (25), 10024–10035.
- (91) Werner, H. J.; Knowles, P. J. An Efficient Internally Contracted Multiconfiguration-Reference Configuration Interaction Method. *J. Chem. Phys.* **1988**, *89* (9), 5803–5814.
- (92) Krishnan, R.; Binkley, J. S.; Seeger, R.; Pople, J. A. Self-Consistent Molecular Orbital Methods. XX. A Basis Set for Correlated Wave Functions. *J. Chem. Phys.* **1980**, *72* (1), 650–654.
- (93) H.-J., W.; Knowles, P. J.; Knizia, G.; Manby, F. R.; Schütz, M.; Celani, P.; Györfy, W.; Kats, D.; Korona, T.; Lindh, R.; et al. MOLPRO, Version 2012, a Packagae of *Ab Initio* Programs.
- (94) Macrae, C. F.; Bruno, I. J.; Chisholm, J. A.; Edgington, P. R.; McCabe, P.; Pidcock, E.; Rodriguez-Monge, L.; Taylor, R.; Van De Streek, J.; Wood, P. A. Mercury CSD 2.0 - New Features for the Visualization and Investigation of Crystal Structures. *J. Appl. Crystallogr.* **2008**, *41* (2), 466–470.
- (95) O’boyle, N. M.; Tenderholt, A. L.; Kangner, K. M. Software News and Updates Cclib: A Library for Package-Independent Computational Chemistry Algorithms. *J. Comput. Chem.* **2007**, *29*, 839–845.
- (96) Barlow, R. B.; Ing, H. R.; Lewis, I. M. The Structure of the Product Formed from Alloxan and O-

Phenylenediamine in the Absence of Acid. *J. Chem. Soc.* **1951**, 0, 3242–3245.

- (97) Schreiber, M.; Silva-Junior, M. R.; Sauer, S. P. A.; Thiel, W. Benchmarks for Electronically Excited States: CASPT2, CC2, CCSD, and CC3. *J. Chem. Phys.* **2008**, 128 (13), 134110–134134.
- (98) Vogler, A.; Kunkely, H. Excited State Properties of Transition Metal Phosphine Complexes. *Coord. Chem. Rev.* **2002**, 230 (1–2), 243–251.
- (99) Barbieri, A.; Accorsi, G.; Armaroli, N. Luminescent Complexes beyond the Platinum Group: The d¹⁰ Avenue. *Chem. Commun.* **2008**, 0 (19), 2185–2193.
- (100) Coughlin, F. J.; Oyler, K. D.; Pascal, R. A.; Bernhard, S. Determination of Absolute Configuration of Chiral Hemicage Metal Complexes Using Time-Dependent Density Functional Theory. *Inorg. Chem.* **2008**, 47 (3), 974–979.
- (101) Mirzaei, M.; Hassanpoor, A.; Alizadeh, H.; Gohari, M.; Blake, A. J. An Eight-Coordinate Zinc Complex Containing the Highly Pre-Organized Ligand 1,10-Phenanthroline-2,9-Dicarboxylic Acid: Solvothermal Synthesis, Supramolecular Structure and CSD Studies. *J. Mol. Struct.* **2018**, 1171 (2), 626–630.
- (102) Kasha, M. Characterization of Electronic Transitions in Complex Molecules. *Discuss. Faraday Soc.* **1950**, 9, 14–19.
- (103) Aquino, A. J. A.; Lischka, H.; Hättig, C. Excited-State Intramolecular Proton Transfer: A Survey of TDDFT and RI-CC2 Excited-State Potential Energy Surfaces. *J. Phys. Chem. A* **2005**, 109 (14), 3201–3208.
- (104) Louant, O.; Champagne, B.; Liégeois, V. Investigation of the Electronic Excited-State Equilibrium Geometries of Three Molecules Undergoing ESIPT: A RI-CC2 and TDDFT Study. *J. Phys. Chem. A* **2018**, 122 (4), 972–984.
- (105) Ho, K.-Y.; Yu, W.-Y.; Cheung, K.-K.; Che, C.-M. A Blue Photoluminescent [Zn(L)(CN)₂] (L = 2,2'-Dipyridylamine) Material with a Supramolecular One-Dimensional Chain Structure. *Chem. Commun.* **1998**, 3 (19), 2101–2102.
- (106) Ho, K.-Y.; Yu, W.-Y.; Cheung, K.-K.; Che, C.-M. Blue Luminescent Zinc(II) Complexes with Polypyridylamine Ligands: Crystal Structures and Luminescence Properties. *J. Chem. Soc. Dalton Trans.* **1999**, 14, 1581–1586.

- (107) Liu, Q.-D.; Wang, R.; Wang, S. Blue Phosphorescent Zn(II) and Orange Phosphorescent Pt(II) Complexes of 4,4'-Diphenyl-6,6'-Dimethyl-2,2'-Bipyrimidine. *Dalt. Trans.* **2004**, 35, 2073–2079.
- (108) Evans, R. C.; Douglas, P.; Winscom, C. J. Coordination Complexes Exhibiting Room-Temperature Phosphorescence: Evaluation of Their Suitability as Triplet Emitters in Organic Light Emitting Diodes. *Coord. Chem. Rev.* **2006**, 250 (15–16), 2093–2126.
- (109) Omary, M. A.; Rawashdeh-Omary, M. A.; Diyabalanage, H. V. K.; Dias, H. V. R. Blue Phosphors of Dinuclear and Mononuclear Copper(I) and Silver(I) Complexes of 3,5-Bis(Trifluoromethyl)Pyrazolate and the Related Bis(Pyrazolyl)Borate. *Inorg. Chem.* **2003**, 42 (26), 8612–8614.
- (110) Yam, V. W. W.; Cheng, E. C. C. Highlights on the Recent Advances in Gold Chemistry-a Photophysical Perspective. *Chem. Soc. Rev.* **2008**, 37 (9), 1806–1813.

Chapter 4: General Conclusion

In this thesis, I have carried out theoretical computations to approach the photophysical properties and excited states of the metal complexes, i.e., metal-organic hybrid molecules. The metal complexes show both fluorescence and phosphorescence, unlike organic and inorganic molecules. In particular, I focused on the metal complexes which shows multiple-emissions. The multiple-emissions are mainly explained by two different mechanisms. In the first mechanism, not only the lowest but also the higher excited states contribute to emission against the Kasha's rule; such a case occurs when the internal conversion to the lower excited state is slow because of a large energy gap. In the second mechanism, emission is originated from several minima in the lowest excited states due to intra- and inter-molecular interactions, obeying the Kasha's rule. To design the metal complexes accompanying the multiple-emissions, it is significant to explore the excited state potential energy surfaces and emission mechanisms by theoretical approaches.

In Chapter 2, I worked on the excited states and multiple-emission mechanism of a thiolate protected Au₂₅ cluster, [Au₂₅(SR)₁₈]⁻ (R = Me, EtPh: methyl, phenylethyl), as an example of the multiple-emissions preventing the Kasha's rule. According to the experimental report, [Au₂₅(SR)₁₈]⁻ (R = Me, EtPh) shows multiple photoluminescence with peaks in the range of 1 ~ 1.8 eV and around 2.5 eV with marginal effects of the surface ligand. To examine the emission mechanism of multiple-emissions at 1.1, 1.55 and 2.48 eV, geometry optimizations were carried out for the ground and excited states by DFT and TD-DFT methods. After geometry optimization for the S₁ state, I found that the estimated emission energy corresponds to the photoluminescence at 1.1 eV, which is in good agreement with a previous report. I focused on the S₇ state because there is substantial energy gap between S₆ and S₇ states in the ground state structure. After geometry optimization for the S₇ state, two minima, denoted as S_{7MIN}^{em} and S_{7MIN}^{non}, were obtained. The S_{7MIN}^{non} corresponds to a P to D intraband transition and is energetically close to the S₆ state, whereas the S_{7MIN}^{em} is a d,p to D interband transition and has a large energy gap between the S₆ and S₇ state. I proposed that the emission at 2.48 eV originates from the S_{7MIN}^{em} state. The S₇ state has two different excited state characters, and these different excited state characters play an important role in the multiple-emissions.

In Chapter 3, to investigate the mechanism of multiple-emissions relating to several minima, I focused on the Zn-hqxc complex whose photoluminescence is associated with ESIPT through intramolecular hydrogen bonds. hqxcH does not show the ESIPT emission, while the Zn-hqxc complex shows the ESIPT emission. The present calculations indicate that the ESIPT emission is caused by the structural change from the Lactam form to the Enol form via coordination zinc atom. Also, the emission of the Zn-hqxc complex is suggested to be from the S_{1MIN} (Keto-Enol, $\pi\pi^*$), the T_{1MIN} (Enol-Enol, $\pi\pi^*$), and the T_{1MIN} (Keto-Keto, $\pi\pi^*$), and not only fluorescence but also phosphorescence could be enhanced by the non-negligible spin-orbit effect. The photophysical properties of Zn-hqxc complex are mainly ascribed to the hqxc ligand (ligand-centered, LC). Thus, I suggested that new metal complexes with the ESIPT emission can be developed if the molecule is designed to show a LC emission mainly as well as the Zn-hqxc complex. For the metal complex with the LC emission, one can choose d^{10} metal complexes of Au(I), Ag(I), and Cu(I), as well as cyclometalated Pt(II) and Ir(III) complexes.

In this thesis, I challenged to approach theoretically for metal complexes having the multiple-emissions ascribed to two different factors. In the case preventing Kasha's rule such as the thiolate protected Au₂₅ cluster, it could be important to make different excited state characters with large energy gap in higher excited states. In the other case obeying the Kasha's rule such as the Zn-hqxc complex with the ESIPT emission, the LC emission is one of the keys to make the multiple-emissions based on the ESIPT. I believe that the present results prompt elucidation of other metal complexes and molecular designs for the multiple-emissions and the chemical applications.

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