

# Proton transfer processes and luminescence of ESIPT-capable zinc(II) complexes with imidazole and pyrimidine ligands

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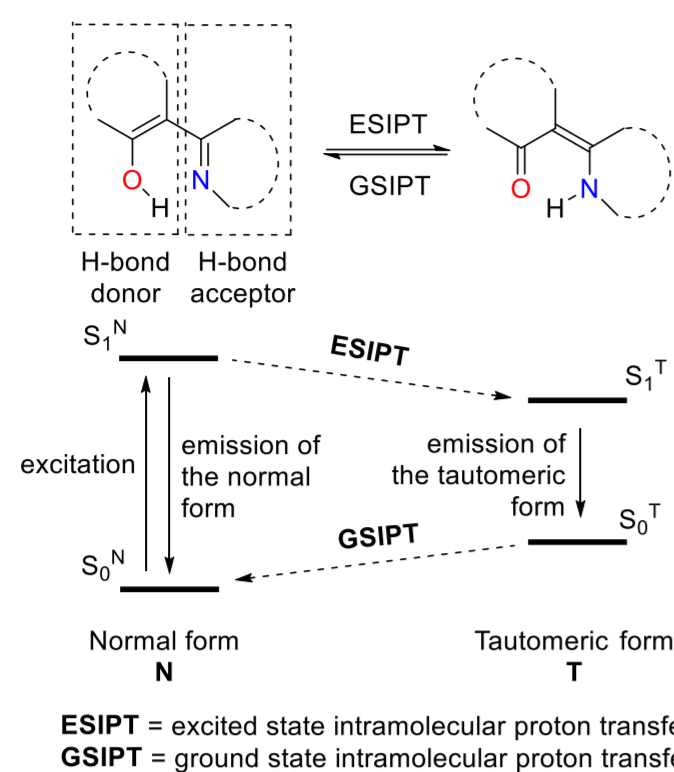
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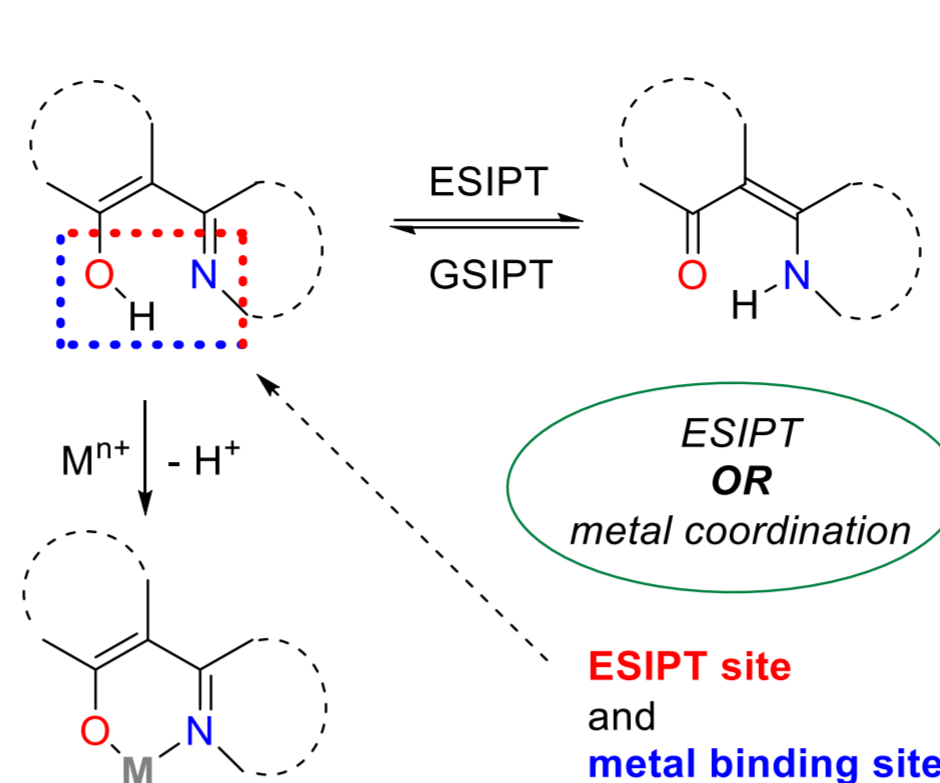
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## Excited state intramolecular proton transfer

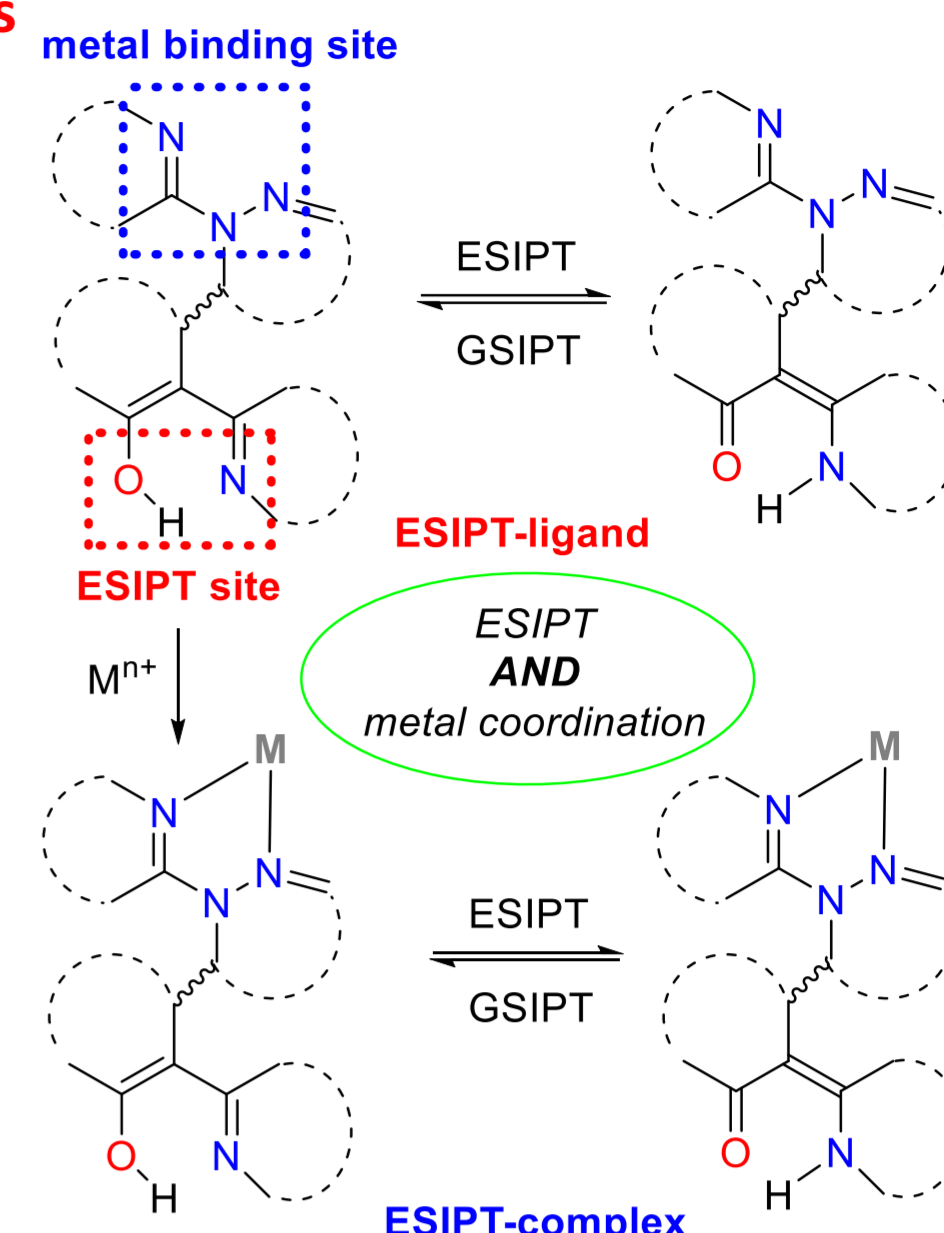


Excited state intramolecular proton transfer (ESIPT) is one of fundamental processes for natural sciences. The ESIPT reaction follows the excitation of a molecule featuring a short intramolecular hydrogen bond and affords a tautomeric form in its excited state. The emission of the tautomeric form leads to large Stokes shifts of ca. 150 - 200 nm. Ground state intramolecular proton transfer (GSIPT) closes the photocycle

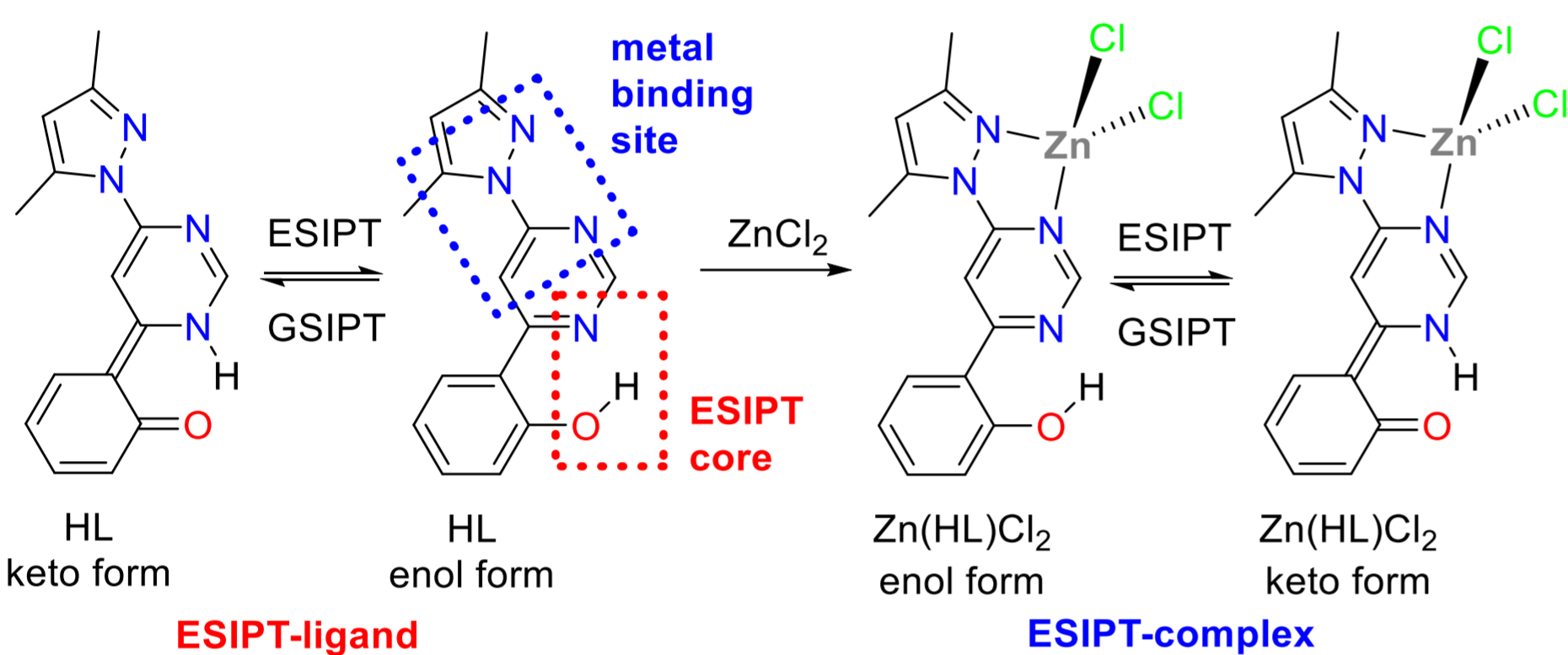
## ESIPT and metal binding as competing or concomitant processes



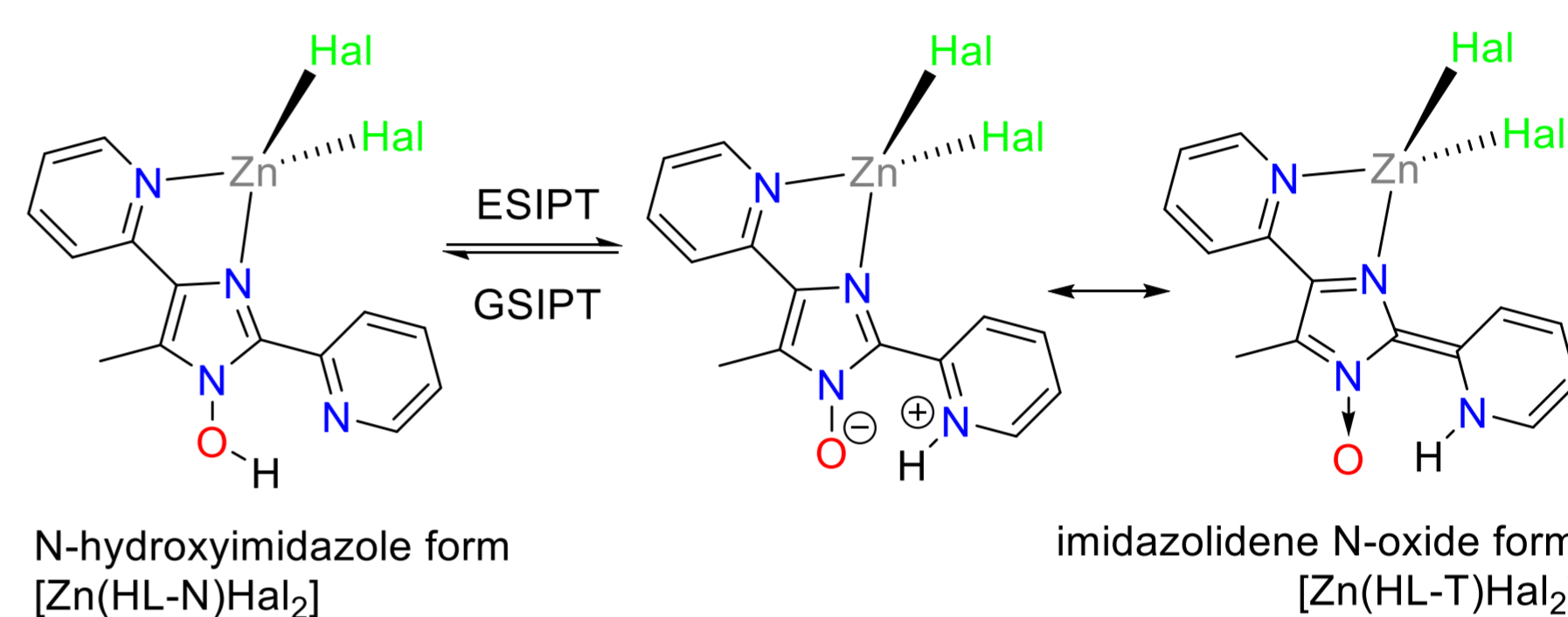
The interaction of ESIPT-fluorophores with metal ions leads to the deprotonation of the ESIPT site due to the coordination of metal ions. To study the impact of coordinated metal ions on the ESIPT reaction, two separate sites, namely the ESIPT site and a metal binding site, need to be rationally designed in a single ESIPT-fluorophore molecule.



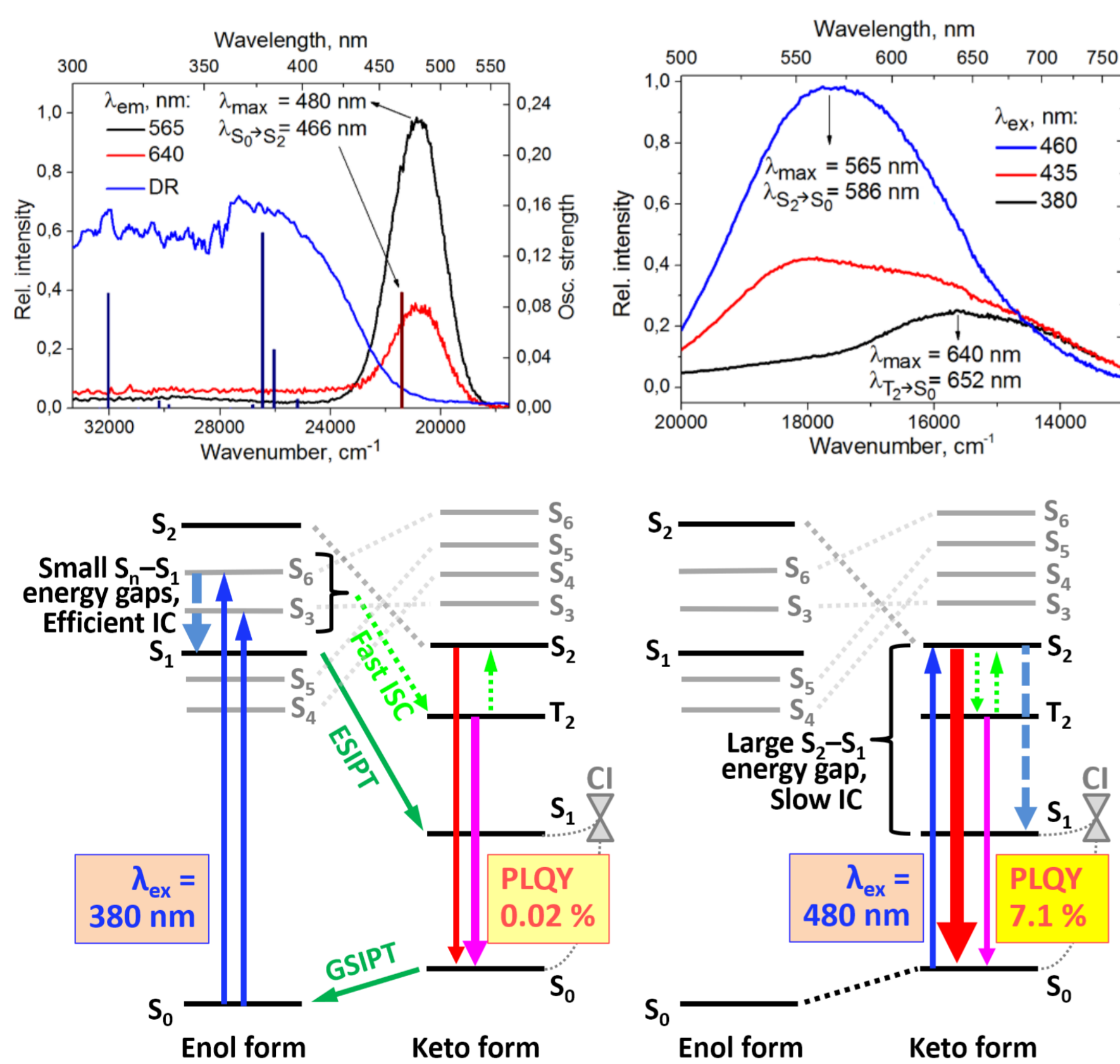
## Pyrimidine-based ESIPT-capable complexes



## Imidazole-based ESIPT-capable complexes

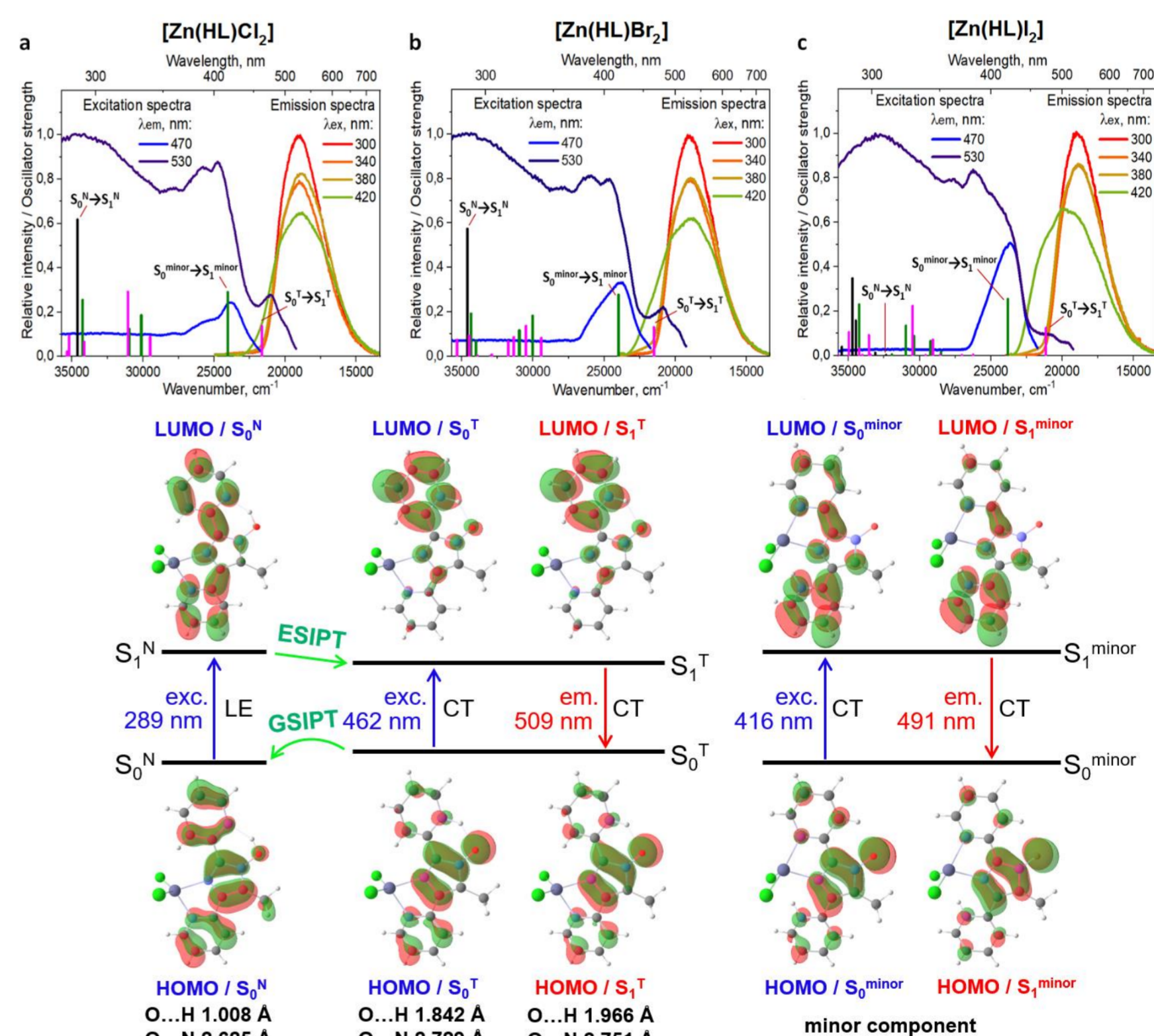


## Emission of pyrimidine-based ESIPT-capable complexes



The ESIPT process in HL and [Zn(HL)Cl<sub>2</sub>] is barrierless and thermodynamically favorable in the  $S_1$  and  $S_2$  states. HL and [Zn(HL)Cl<sub>2</sub>] demonstrate abnormal anti-Kasha fluorescence ( $S_2 \rightarrow S_0$ ) and anti-Kasha phosphorescence ( $T_2 \rightarrow S_0$ ) associated with relatively low  $S_2 \rightarrow S_1$  and  $T_2 \rightarrow S_1$  internal conversion rates. Energetically achievable  $S_1/S_0$  and  $T_1/S_0$  intersections are responsible for the fast non-radiative decay of the  $S_1$  and  $T_1$  states. Quasi-intersections of the  $S_2$  and  $T_2$  state potential energy surfaces facilitate thermally activated delayed fluorescence (TADF,  $T_2 \rightarrow S_2 \rightarrow S_0$ ) for both compounds. The molecules of [Zn(HL)Cl<sub>2</sub>] can be trapped and photoexcited from the local minimum of the  $S_0$  state in the tautomeric keto form, which results in an anomalously small apparent Stokes shift of 90 nm. The absence of such minimum on the ground state potential energy surface of HL leads to a considerably larger Stokes shift of 165 nm.

## Emission of imidazole-based ESIPT-capable complexes



A series of ESIPT-capable zinc(II) complexes [Zn(HL)Hal<sub>2</sub>] (Hal = Cl, Br, I) with a rationally designed ESIPT-ligand 1-hydroxy-5-methyl-2,4-di(pyridin-2-yl)-1H-imidazole (HL) featuring spatially separated metal binding and ESIPT sites has been synthesized and characterized. Crystals of these compounds consist of a mixture of two isomers of [Zn(HL)Hal<sub>2</sub>], major of which has a short intramolecular hydrogen bond O-H...N as a pre-requisite for ESIPT. In the solid state, the complexes [Zn(HL)Hal<sub>2</sub>] demonstrate temperature- and excitation wavelength dependent fluorescence in the cyan region due to the interplay of two intraligand fluorescence channels with excited state lifetimes spanning from 0.2 to 4.3 ns. The coordination of HL by Zn<sup>2+</sup> ions results in the increase in the photoluminescence efficiency, and the photoluminescence quantum yields (PLQY) for the complexes reach 12% at  $\lambda_{ex} = 300$  nm and 27% at  $\lambda_{ex} = 400$  nm in comparison with the PLQY of free HL of ca. 2%. Quantum chemical calculations indicate that the N-hydroxy - N-oxide phototautomerization is both thermodynamically and kinetically favourable in the  $S_1$  state for [Zn(HL)Hal<sub>2</sub>]. The proton transfer induces a considerable geometrical reorganization and therefore results in large Stokes shifts of ca. 230 nm.

## References

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