A novel non-fluorescent excited state intramolecular proton transfer phenomenon induced by intramolecular hydrogen bonds: an experimental and theoretical investigation

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Two molecules, 1-hydroxypyrene-2-carbaldehyde (HP) and 1-methoxypyrene-2-carbaldehyde (MP) were explored. We investigated their photophysical properties, using experimental transient absorption and theoretical density functional theory/time-dependent density functional theory (DFT/TDDFT). HP and MP have similar geometric conformations but exhibit entirely different photophysical properties upon excitation into the S₁ state. In contrast to traditional excited state intramolecular proton transfer (ESIPT) in molecules that exhibit either single or dual fluorescence, HP has an unusual non-fluorescent property. Specifically, the ultrafast ESIPT process occurs in 158 fs and is followed by an intersystem crossing (ISC) component of 11.38 ps. In contrast to HP, MP undergoes only an 8 ps timescale process, which was attributed to interactions between solute and solvent. We concluded that this difference arises from intramolecular hydrogen bonds (IMHBs), which induce drastic structural alteration upon excitation.

Compounds that undergo excited state intramolecular proton transfer (ESIPT) have attracted attention¹–⁶ as, for fluorescent probes⁷–⁹, for use in bioimaging¹⁰, as light-emitting materials¹¹, as photostabilizers¹², and in photophysical studies¹³–¹⁷. The characteristic photophysical feature of a molecule undergoing ESIPT is the sub-picosecond timescale and large Stokes shift, which suggest that the structural geometry of the emissive excited state is significantly displaced from that of the ground state¹¹,¹⁷–¹⁹.

Many functional organic molecules exhibiting ESIPT have been investigated¹⁹–²⁴. Furthermore, numerous studies have demonstrated that the ESIPT process involves a heterocyclic ring containing a hydroxyl-group and a neighbouring proton acceptor that can form IMHBs²²,²⁵. Recently, it was found that intramolecular hydrogen bonding plays a crucial role in the proton transfer process²⁶. The ESIPT process can be facilitated by the excited-state intramolecular hydrogen bond strengthening in the S₁ state²⁶,²⁷. The first ESIPT investigation, which was performed on methyl salicylate (MS) by Weller²⁸, demonstrated that MS is a three energy level system containing the ground state, a normal excited state, and a tautomer excited state, and it is the tautomerism that produces dual fluorescence.

However, despite numerous investigations since that of Weller, the ESIPT process still presents challenges both theoretically and experimentally due to the intrinsically complex physical and chemical nature, such as the cleavage and formation of hydrogen bonds and the subsequent nuclear rearrangement with inversion. More recently, experiments by Mitra et al.²⁹ showed that the ultrafast ESIPT of 4-methyl-2,6-diformyl phenol occurs at
approximately 200 fs in cyclohexane followed by an intramolecular vibrational redistribution (IVR) process for approximately 2.8 ps before emitting fluorescence from the ESIPT state. Tang et al. investigated the ESIPT process of 7-hydroxy-1-indanone and its derivatives by theoretical and experimental methods, elaborating the details of the synthesis, photophysical properties, and OLED application. In our previous report, we theoretically investigated the salicylaldehyde (SA) molecule, which has exclusively intramolecular O–H⋯O hydrogen bonds that form a strong quasi-aromatic chelating ring. We found that the hydrogen bonded quasi-aromatic chelating ring in the excited state becomes smaller, which facilitates the ESIPT process. We also discovered that SA exhibits single fluorescence, which unlike the mechanism described by Weller. We believe that the ESIPT system under the effect of IMHBs can exhibit non-fluorescence in addition to single and dual fluorescence. Therefore, we focused on the ESIPT system HP, which was found to be non-fluorescent in the S1 state. We also investigated MP molecule, which cannot form IMHBs, for comparison.

The six-membered, intramolecularly hydrogen-bonded system HP is an ideal model to explore the effect of IMHBs on the ESIPT system. To shed light on the ESIPT dynamics of HP, we report a combined experimental and theoretical method to investigate the HP and MP molecules and to confirm experimental results and discover more detailed information.

Results and Discussion

The structures of the HP (a) and MP (b) molecules are shown in Fig. 1. An IMHB can be formed between the carbonyl group oxygen and the hydroxyl hydrogen in the HP molecule to create a hydrogen-bonded, quasi-aromatic chelating ring. In contrast, the IMHB is not formed in the MP molecule. Figure 1 also depicts the steady-state absorption and fluorescence spectra of HP (a) and MP (b) in cyclohexane (CHX). The absorption spectra show different vibronic structures between HP and MP, which indicates that the maxima of the absorption bands of HP and MP are located near 455 and 417 nm, respectively. The width of the absorption band for HP is broader than for MP, and the MP band is split more than that of HP. Because the two molecules have similar geometric conformations, we suggest that the obvious difference in absorption is caused by IMHBs. The fluorescence peak of MP is at 438 nm. Upon 400 nm excitation, HP is non-fluorescent, which is different from dual-fluorescent MS investigated by Weller.

We performed femtosecond transient absorption spectroscopy to investigate the excited state properties of HP and MP in CHX. Figure 2 depicts the 3D image plot of transient absorption for HP (a) and MP (b) in CHX after excitation at 400 nm.
wavelength and time delay after excitation. For HP (Fig. 2a), there are two main components, absorption (positive signal) at approximately 520 nm and emission (negative signal) at approximately 450 nm. For MP (Fig. 2b), the absorption is at approximately 500 nm, and the emission is at approximately 460 nm. However, in contrast to HP, the lifetime of the absorption at approximately 500 nm is relatively longer, and the absorption width is relatively narrower for MP. The 3D plot shows a global overview of the excited dynamics of HP and MP.

The transient positive and negative differences in absorbance values, which evolve over delay time after excitation at 400 nm, are shown in Fig. 3. Figure 3(a,b) depict the transient absorption spectra of the HP molecule at different delay times. Initially, an emission band at approximately 455 nm appears and ends within hundreds of femtoseconds with a slight blue-shift. In the meantime, a broad absorption band appears, and the shape of the transient absorption spectra is changed with time. Before 1.2 ps, the characteristic peak of the absorption band has an obvious red shift from 470 nm to 520 nm, and the intensity and the width of the absorption band increase with time. After 1.2 ps, the intensity and width of the absorption band begin to decrease, and the characteristic peak has a slight blue-shift from 520 nm to 502 nm that evolves over delay time. In contrast, the time evolution of the transient absorption spectra of MP is shown in Fig. 3(c,d). It takes less time to reach the maximum intensity of absorption, and the width is narrower for MP than HP at the same delay time. Moreover, in the range of 0 to 1 ps, the characteristic peak absorption band has a relatively smaller red-shift from 470 nm to 502 nm compared to that of HP. The rate of the absorption intensity decrease is much slower than that of the HP molecule and is without the blue-shift of the characteristic peak.

To investigate the lifetime of the dynamics processes for HP and MP, a global fit analysis was used, in which sets of kinetic curves were fit simultaneously using exponential components with common lifetimes (Table 1).

| System | $\tau_1$ (fs) | $\tau_2$ (ps) |
|--------|---------------|---------------|
| HP     | 158.6 ± 19.12 (12.06%) | 11.38 ± 2.859 (25.12%) |
| MP     | —             | 8.42 ± 0.765 (9.09%) |

Table 1. Transient absorption kinetics lifetimes of HP and MP in CHX solvent by global analysis. The meaning of the proportion is the deviation percentage.
Through our experimental investigation, we explored how the HP molecule is different from the MP molecule. The HP molecule exhibits a dual ultrafast process and non-fluorescence emission during excitation at 400 nm, but MP exhibits just one ultrafast process and fluorescence emission. To reveal the mechanism of this phenomenon, we performed theoretical analyses using DFT and TDDFT.

Table 2 shows the calculated absorption and emission peaks of the HP and MP molecules using the TDDFT/B3LYP/TZVP method. The absorption spectrum is calculated by vertical excitation from the ground state to the S1 state, and the emission spectrum is calculated by emission from the S1 state equilibrium geometry to the ground state non-equilibrium geometry. The theoretical results are in good agreement with the experimentally measured absorption and emission maxima, which suggests that the method is effective and credible. Moreover, the small Stokes shift of MP suggests that its primary de-excitation process is fluorescence.

To investigate the mechanism of de-excitation for HP, we optimized the geometric conformations of the enol (S0), enol* (S1) and keto* (S1) forms and the results are shown in Fig. 4. These optimized geometries show that the IMHB of HP is formed between C17=O2 and O1–H10 in the enol and enol* form, whereas an IMHB can be formed between C2=O1 and O2–H10 in the keto* form. In addition, the numerical values of the key geometric parameters of different electronic states can be found in supplementary Table S1. Based on the results of the geometric conformations, we found that HP exhibits an ESIPT process corresponding to the fs timescale in our experiment. Upon excitation to enol*, the distance between O2 and H10 decreases from 1.733 Å to 1.447 Å, whereas the bond length between O1 and H10 increases from 0.988 Å to 1.063 Å, which suggests that H10 has the tendency to approach O2 and depart from O1. Eventually, HP evolves into the keto* state. The intramolecular C17=O2 ⋅⋅⋅H10–O1 hydrogen bond breaks, concomitantly with the formation of an intramolecular C2=O1 ⋅⋅⋅H10–O2 hydrogen bond. The keto* state bond angles C17C1C2 and C1C2O1 are both smaller than the corresponding ground state bond angles, and the keto* state distance between O1 and O2 becomes shorter than the corresponding ground state distance, which indicates that the hydrogen-bonded quasi-aromatic chelating ring becomes smaller after excitation. Moreover, we found that the IMHB becomes short and that H10 transfers from O1 to O2. The interactions of involved atoms increase when the distances between atoms decrease. Compared to HP, MP cannot form IMHBs in the ground state or in the S1 state due to the lack of a hydrogen donor, such as the hydroxyl hydrogen atom of HP, as shown in Fig. 5. Therefore, we concluded that intramolecular hydrogen bonding in the HP molecule facilitates the ESIPT process. In contrast to the complexity of HP, the geometric conformation of MP is much simpler. There is no obvious structural alteration between S0 and S1, which indicates that MP molecules do not exhibit specific ultrafast processes such as ESIPT and twisted intramolecular charge transfer (TICT), during the de-excitation.

To demonstrate the details of the ESIPT process of HP and to explore the non-fluorescent mechanism of HP upon excitation to the S1 state, we calculated potential energy curves in different electronic states. The potential energy curves of HP were optimized by fixing the distance between O1 and H10 (proton transfer coordinate) at different values, which are recorded in Fig. 6. There is only one stable geometry in the S0 state, which is associated

| System | Abs. (Thero.) | Abs. (Exp.) | Fluo. (Thero.) | Fluo. (Exp.) |
|--------|--------------|-------------|---------------|-------------|
| HP     | 442          | 455         | --            | --          |
| MP     | 405          | 417         | 430           | 438         |

Table 2. Calculated absorption peak and emission peak of the HP and MP molecules compared with the experimental data (unit: nm).
with the enol form. The potential energy curves reveal that the stable points in the S₁ state correspond to the coordinates 1.063 Å (enol* form) and 1.540 Å (keto* form), respectively. HP has two stable equilibrium geometries after Frank-Condon transition to the S₁ state. To achieve the equilibrium geometry of the S₁ state tautomer form, H₁₀ transfers from O₁ to O₂ and forms the new hydrogen bond C₂─O₁⋅⋅⋅H₁₀─O₂. The existence of the S₁ state tautomer equilibrium geometry is direct evidence of an ESIPT process with photoexcitation to the S₁ state. The calculation of the electronic excitation energy of HP shown in Table 3 indicates that the energy of the 1st and 2nd triplet states (T₁ and T₂) are lower than that of the S₁ state, and the energy of the 3rd triplet state (T₃) is higher than that of the S₁ state. Therefore, we also calculated the potential energy curves of the T₁ and T₂ states, as shown in Fig. 6. There is no cross point between S₁ and T₁. The occurrence of a cross between S₁ and T₂ is at approximately 1.5 Å to 1.6 Å, which corresponds to the coordinate of the S₁ keto* state, i.e., the ISC process occurs between the S₁ and T₂ states. Therefore, combined with the non-fluorescent excitation to the S₁ state, we concluded that the relaxation pathway of HP after ESIPT is the ISC process from the S₁ keto* to the T₂ state²⁹–³¹. Comparing

|   | E (nm) | OS  |
|---|--------|-----|
| T₃ | 381    | 0.018 |
| S₁ | 442    | 0.052 |
| T₂ | 544    | 0.270 |
| T₁ | 600    | 0.989 |

Table 3. The electronic excitation energy (E) corresponding to the oscillator strength (OS) for low-lying electronically excited states of HP.
with the results of Weller’s, we can find that both HP and MS have two stable equilibrium geometries after Frank-Condon transition to the S1 state. Differently, MS exhibits stepwise dual fluorescence from two stable equilibrium geometries of the S1 state, and HP is non-fluorescent due to the ISC process from the S1 keto* state to the T2 state after the ESIPT process.

The vibrational frequencies of the stretching vibrations of C=O and O–H groups that are involved in hydrogen bonds can provide a specific signature of the hydrogen-bonding dynamics. In the present work, we calculated the IR spectra (B3LYP/TZVP, scaling factor 0.9630) of HP at the S0, S1 states (enol* and keto* forms). The calculated IR spectra of the ground state and S1 state in the spectral range from 1400 to 3500 cm⁻¹ are shown in Fig. 7, which contains not only the characteristic peaks of the O1–H10 group of the S0 and S1 normal forms but also the characteristic peaks of the O2–H10 group of the S1 tautomer form. For the S1 tautomer form, the characteristic peaks at approximately 3213 cm⁻¹, which is assigned as ν(O1–H10) in S0, and at approximately 2113 cm⁻¹, which is assigned as ν(O1–H10) in the enol* form, disappeared, whereas a new characteristic peak appeared at approximately 2492 cm⁻¹ and was assigned as ν(O2–H10). Thus, we can conclude that the O1–H10 bond breaks, and a new O2–H10 bond forms, just as the geometry optimization shows in Fig. 4. Consequently, as auxiliary evidence, the IR spectra correlate well with the result that H10 transfers from O1 to O2 in the S1 excited state. Moreover, corresponding IR spectra of HP at the triplet state can be seen in supplementary Figure S6.

A comparison between the experimental and theoretical results allowed us to understand the properties of the systems more deeply, and the theoretical method gave the experimental results a clear interpretation. We show the mechanism of de-excitation for HP in Fig. 8. First, the HP molecule in the S0 enol state is excited to the S1 enol* state; subsequently, an ESIPT process from the S1 enol* state to the S1 keto* state occurs at a timescale of approximately 158.6 fs. The ISC between S1 and T2 in approximately 11.38 ps gives a reasonable explanation for the non-fluorescence of HP upon excitation into the S1 state. In Fig. 3(a,b), the negative signals below 460 nm for HP molecules correspond primarily to ground state depletion. In the range from 0 to 0.1 ps, because the S1 keto* state is not formed, the characteristic peak at approximately 470 nm is attributed to the S1 enol* state. From 0.1 to 1.2 ps, the observed redshift and intensity increment of the absorption band at approximately 520 nm suggest that the population of the S1 keto* state increases with the relaxation from the hot S1 keto* to the cold S1 keto* state. Between 1.2 and 10 ps, the intensity decrement of the absorption peak at approximately 520 nm arises from the decrement of the population in the S1 keto* state due to the ISC process from S1 keto* to T2 on an approximately 10 ps timescale. This process induces the non-fluorescent property of HP upon excitation to the S1 state. After 10 ps, only the intensity and not the shape of the absorption band changes; thus, the characteristic peak at approximately 502 nm corresponds to the T2 state. Compared with the HP molecule, the de-excitation of MP is
the beam diameter was 2 mm. The sensitivity range was 450–750 nm. All experiments were performed at room intensities were derived from the gradients of the dipole moment. The electronic structure calculations were performed using a 0.5 mm BBO (super-continuum white light, which served as the probe laser. Two laser beams were incident on the sample in the pump laser for exciting samples. The energy per pump pulse at the sample was approximately 3 μJ. DFT and TDDFT34–42 methods, respectively. The B3-LYP (Becke’s three-parameter hybrid exchange function with one set of polarization functions) were used in our DFT and TDDFT calculations 43–46. In addition, the IR spectrum-pure, quality reagent purchased from J&K (China) and was used without further purification. The concentration of HP and MP in CHX was 5×10−6 mol/l. The steady-state absorption and fluorescence spectra were measured with a UV 2550 UV-VIS spectrophotometer and a RF5301 fluorescence spectrophotometer (Shimadzu), respectively.

The steady-state absorption and fluorescence spectra were measured with a UV 2550 UV-VIS spectrophotometer and a RF5301 fluorescence spectrophotometer (Shimadzu), respectively. Transient absorption imaging was based on a femtosecond laser (Coherent Libra, US), which was used as the light source with a power of approximately 4W at 1 kHz repetition rate and a wavelength of 800 nm where the full width at half maximum (FWHM) was 50 fs. The fundamental laser was separated into two beams in a ratio of 9:1. The more intense beam was used for generating the second harmonic (λex = 400 nm) of the fundamental laser using a 0.5 mm BBO (β-BaB2O4, Fujian Castech Crystals Inc., China), which was applied as a pump laser for exciting samples. The energy per pump pulse at the sample was approximately 3 μJ. The other beam passed through a controlled delay line and then focused into a sapphire plate to generate sub-picosecond, super-continuum white light, which served as the probe laser. Two laser beams were incident on the sample in a 0.5 cm quartz cuvette at a small angle (θ ≤ 5°). The fused quartz sample cell was placed in the beam path, and the beam diameter was 2 mm. The sensitivity range for 450–750 nm. All experiments were performed at room temperature (22 °C).

Methods
In the present work, the ground-state and electronic excited-state geometry optimizations were performed by the DFT and TDDFT34–42 methods, respectively. The B3-LYP (Becke’s three-parameter hybrid exchange function with Lee-Yang-Parr gradient-corrected correlation) functional and the TZVP basis sets (the triple-ζ, valence quality with one set of polarization functions) were used in our DFT and TDDFT calculations 43–46. In addition, the IR intensities were derived from the gradients of the dipole moment. The electronic structure calculations were performed using the TURBOMOLE program suite 47.

HP and MP were synthesized according to the literature 48. The cyclohexane (CHX) was a super-dry, spectrum-pure, quality reagent purchased from J&K (China) and was used without further purification. The concentration of HP and MP in CHX was 5×10−6 mol/l.

The steady-state absorption and fluorescence spectra were measured with a UV 2550 UV-VIS spectrophotometer and a RF5301 fluorescence spectrophotometer (Shimadzu), respectively.

Conclusion
In the present exploration, femtosecond transient absorption spectroscopy and DFT/TDDFT were performed to investigate the photoexcitation of HP and MP. We demonstrated that HP exhibits the ESIPT process in the S1 state and discovered the reason for the non-fluorescence of HP upon excitation to the S1 state in CHX. Specifically, the ESIPT process happens in 158 fs, whereas the ISC process occurs on an 11.38 ps timescale. In contrast to HP, MP undergoes an 8 ps timescale process, which was attributed to interactions between the solute and solvent in the S1 state, and it exhibits fluorescence upon excitation to the S0 state. The geometric conformations of HP and MP are similar, but HP differs most from MP in that it is able to form IMHBs. We concluded that the ESIPT and the ISC of HP arise from the existence of IMHBs, which induce drastic structural alterations between the S0 and S1 state.

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Author Contributions
H.Y. and H.L. carried out the experiment. H.Y. performed the theoretical calculation. Y.S. gave the idea of our investigation. G.X., C.Y.R. and H.M.W. executed sample preparation. M.X.J. gave us the technical support. D.J.D. gave us the investigation guidance and helpful discussion.

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