Electronic Supplementary Information

for

Dual Fluorescence of Excited State Intra-molecular Proton Transfer of HBFO: Mechanistic Understanding, Substituent and Solvent Effects

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Section 1, Computational method for rate calculation.

Without consideration of rotational degrees of freedom, the standard expression* for the unimolecular rate constant (units s\(^{-1}\)) of an isolated molecule with total energy \(E\)

\[
k(E) = \frac{N(E)}{2\pi\hbar N_0(E)} \quad \text{(S1)}
\]

Within the separable approximation tunneling is accounted for by replacing \(N(E)\) in eq S1 by \(N_{QM}(E)\)

\[
N_{QM}(E) = \sum_n P(E - \varepsilon_n^\ne)
\]

(S2)

The expression for the unimolecular rate constant which include the effect of tunneling is

\[
k(E) = \frac{\sum_n P(E - \varepsilon_n^\ne)}{2\pi\hbar N_0'(E)} \quad \text{(S3)}
\]

Where \(N(E)\) and \(N_0(E)\) are the integral densities of states of the transition state and the reactant molecule. The expressions of them are as follows:

\[
N(E) = \sum_n h(E - \varepsilon_n^\ne) \quad \text{(S4)}
\]

\[
N_0(E) = \sum_n h(E - \varepsilon_n) \quad \text{(S5)}
\]

Where \(h(x)\) is the usual step-function

\[
h(x) = \begin{cases} 0, & x < 0 \\ 1, & x > 0 \end{cases} \quad \text{(S6)}
\]

And \(\varepsilon_n^\ne\) and \(\varepsilon_n\) are the vibrational energy levels of the transition state and the reactant molecule. It is generally to assume the vibrational energy levels are almost given by an oscillator approximation, so the expression can be obtained as follows:

\[
\varepsilon_n = \sum_{i=1}^{s} \hbar \omega_i \left( n_i + \frac{1}{2} \right) \quad \text{(S7)}
\]

\[
\varepsilon_n^\ne = V_0 + \sum_{i=1}^{s-1} \hbar \omega_i^\ne \left( n_i + \frac{1}{2} \right) \quad \text{(S8)}
\]
Where \( s \) is the number of vibrational degrees of freedom of the stable molecule, \( \{\omega_i\} \) and \( \{\omega_i^\pi\} \) are the normal mode vibration frequencies for the transition state and for the reactant molecule, respectively. And \( V_0 \) is the energy of the saddle point of the PES relative to the minimum PES of the reactant molecule, the total energy \( E \) is based on the relative energy compares to the minimum of the PES.

Next the large sums of the densities of states would be disposed approximately. So the expressions are shown below:

\[
N_0(E) = \frac{E^s}{s! \sum_{i=1}^{s} (\hbar \omega_i)} \quad \text{(S9)}
\]

\[
N(E) = \frac{(E-V_0)^{s-1}}{(s-1)! \sum_{i=1}^{s-1} (\hbar \omega_i^\pi)} \quad \text{(S10)}
\]

On the basis of above approximates, the expression of the rate constant can be expressed as follow.

\[
k(E) = A \left( \frac{E-V_0}{E} \right)^{s-1} \quad \text{(S11)}
\]

where \( A \) is a frequency factor (units \( s^{-1} \)).

\[
A = \left\{ \prod_{i=1}^{s} \omega_i \right\} \div \left\{ 2\pi \prod_{i=1}^{s-1} \omega_i^\pi \right\} \quad \text{(S12)}
\]

The unit conversion from cm\(^{-1}\) for normal mode vibration frequencies and frequency factor \( A \) to rate unit \( s^{-1} \) is taken by using the following formula

\[
C = \frac{\nu}{\bar{\nu}} \quad \text{(S13)}
\]

Where \( \nu \) is the unimolecular vibration frequencies, \( \bar{\nu} \) is the wave number and \( c \) is the velocity of light.

Therefore, the expression of frequency factor can be written as follows:

\[
A = \left\{ \prod_{i=1}^{s} \omega_i \right\} \times \left( 3 \times 10^{10} \right) \div \left\{ 2\pi \prod_{i=1}^{s-1} \omega_i^\pi \right\} \quad \text{(S14)}
\]
So finally the expression of unimolecular rate constant can be expressed as:

\[
k(E) = \frac{\prod_{i=1}^{s} \omega_i \times (3 \times 10^{10})}{2\pi \prod_{i=1}^{s-1} \omega_i} \left( \frac{E - V_0}{E} \right)^{s-1}
\]

(S15)
Section 2, Test calculations for the choice of most appropriate active space of HBFO at the CASSCF/CASPT2 level of theory.

Test 1:

The vertical excitation energy: 3.31 eV (experimental value: 3.03 eV)

The diagram of orbitals in active space cas(10,9)

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<tr>
<th>Occupation numbers of these orbitals</th>
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<tbody>
<tr>
<td>1 0.199988D+01</td>
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<tr>
<td>2 0.321563D-04 0.199989D+01</td>
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<tr>
<td>3 -0.973261D-07 0.110158D-05 0.198126D+01</td>
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<tr>
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<tr>
<td>6 0.582563D-04 0.101117D-04 0.300263D-06 0.333791D-03 -0.136028D-03</td>
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<tr>
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<tr>
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Test 2

The vertical excitation energy: 3.97 eV (experimental value: 3.03 eV)

The diagram of orbitals in active space cas(10,9)

Occupation numbers of these orbitals

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**Test 3**

The vertical excitation energy: 3.88 eV (experimental value: 3.03 eV)

The diagram of orbitals in active space cas(10,8)

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<tr>
<td>8 0.198506D-04</td>
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Section 3, Figures

Figure S1. The diagram of selected orbitals in active space for HBFO.

- π orbital
- π* orbital
- π orbital
- π* orbital
- π orbital
- π* orbital
- O-H σ orbital
- O-H σ* orbital

n orbital (C=O)
Figure S2. The diagram of selected orbitals in active space for meta-CF₃-HBFO.

- $\pi$ orbital
- $\pi^*$ orbital
- $\pi$ orbital
- $\pi^*$ orbital
- O-H $\sigma$ orbital
- O-H $\sigma^*$ orbital
- $n$ orbital (F)
- $n$ orbital (C=O)
Figure S3. The diagram of selected orbitals in active space for *meta*-NH$_2$-HBFO.

- $\pi$ orbital
- $\pi^*$ orbital
- $\pi$ orbital
- $\pi^*$ orbital
- $\pi$ orbital
- $\pi^*$ orbital
- O-H $\sigma$ orbital
- O-H $\sigma^*$ orbital
- $n$ orbital (N)
- $n$ orbital (C=O)
Section 4, Tables

Table S1 The vertical excitation energies ($E_\perp$, eV), wavelengths ($\lambda_{\text{cal}}$, nm), experimental wavelength ($\lambda_{\text{exp}}$, nm), oscillator strengths ($f$), dipole moments (D.M., Debye) and the character of singly occupied orbitals in the $S_{\text{CT}}(1\pi\pi^*)$ state for the Franck-Condon structures of HBFO at the CASPT2//CAS(10,9)/6-31G* and for meta-CF$_3$-HBFO, meta-NH$_2$-HBFO, para-CF$_3$-HBFO, para-NH$_2$-HBFO at the CASPT2//CAS(12,10)/6-31G* level of theory.

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<tr>
<th>Fluorescers</th>
<th>Singly occupied orbitals</th>
<th>D.M.</th>
<th>$f$</th>
<th>$E_\perp$</th>
<th>$\lambda_{\text{cal}}$</th>
<th>$\lambda_{\text{exp}}$</th>
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Table S2 The absolute energy (A.E.) in Hartree for the optimized structures of enol (E)/keto(K) forms and maxima of five fluorescers, HBFO, meta-CF$_3$-HBFO, meta-NH$_2$-HBFO, para-CF$_3$-HBFO, para-NH$_2$-HBFO in gas phase, cyclohexane and acetonitrile solvents along ESIPT pathways in the $S_{\text{CT}}(1\pi\pi^*)$ state obtained at CASPT2//CASSCF/6-31+G* or CASPT2//CASSCF/PCM/6-31+G* level of theory.

<table>
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<th>Solvents</th>
<th>critical points</th>
<th>A.E.</th>
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<tr>
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S12
Table S3: The comparisons between transition states (maxima) structure and the absolute energy (A.E.) in Hartree at CASPT2 level for HBFO, meta-CF<sub>3</sub>-HBFO, meta-NH<sub>2</sub>-HBFO in the S<sub>CT</sub>(<sup>1</sup>ππ*) state are obtained by constraint geometry method and traditional TS optimizations, respectively.

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<th>TS optimization</th>
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Table S4 (a) The fragment of charge translocation from the moieties of naphthalene (Q1) to carbonyl group (Q2) and benzene (Q3) (b) The sum of Mulliken charge distribution of the different fragment upon $S_0\rightarrow S_{CT}(^1\pi\pi^*)$ FC excitation of HBFO.

Table S5 The test computations of single energy calculation at the CASPT2/6-31+G* level of theory along the selective stationary points that are adjacent to maxima of HBFO, meta-CF$_3$-HBFO and meta-NH$_2$-HBFO to confirm the reliability of the maxima searching.
Section 5-1, Cartesian coordinates of the optimized structures for HBFO along the ESIPT reaction pathway in S\textsubscript{CT}(1\pi^* ) state at the CAS(10e/9o)/6-31G* level of theory.

S\textsubscript{CT}(1\pi^*)-E

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S16
Section 5-2, Cartesian coordinates of the optimized structures for meta-CF$_3$-HBFO along ESIPT reaction pathway in S$_{\text{CT}}$(1$\pi\pi^*$) state at the CAS(12e/10o)/6-31G* level of theory.

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S21
Section 5-4, Cartesian coordinates of the optimized structures for para-CF₃-HBFO along ESIPT reaction pathway in $S_{\text{CT}}(^{1}\pi\pi^*)$ state at the CAS(12e/10o)/6-31G* level of theory.

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S23
Section 5-5, Cartesian coordinates of the optimized structures for para-NH$_2$-HBFO along ESIPT reaction pathways in $S_{\text{CT}}(^1\pi\pi^*)$ state at the CAS(12e/10o)/6-31G* level of theory.

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