New Insights into the Dual Fluorescence of Methyl Salicylate: Effects of Intermolecular Hydrogen Bonding and Solvation

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ABSTRACT: In this paper, we propose a new and complete mechanism for dual fluorescence of methyl salicylate (MS) under different conditions using a combined experimental (i.e., steady-state absorption and emission spectra and time-resolved fluorescence spectra) and theoretical (i.e., time-dependent density function theory) study. First, our theoretical study indicates that the barrier height for excited state intramolecular proton transfer (ESIPT) reaction of ketoB depends on the solvent polarity. In nonpolar solvents, the ESIPT reaction of ketoB is barrierless; the barrier height will increase with increasing solvent polarity. Second, we found that, in alcoholic solvents, intermolecular hydrogen bonding plays a more important role. The ketoB form of MS can form two hydrogen bonds with alcoholic solvents; one will facilitate ESIPT and produce the emission band in the blue region; the other one precludes ESIPT and produces the emission band in the near-UV region. Our proposed new mechanism can well explain previous results as well as our new experimental results.

INTRODUCTION

About 50 years ago, the dual fluorescence of methyl salicylate (MS) was first observed by Weller.1,2 Since then, a large number of experimental and theoretical studies3–21 have been devoted to investigating the mechanism of the dual fluorescence of MS. The two emission bands of MS are around 350 and 440 nm and are usually denoted as the near-UV and the blue band, respectively. It seems that there is no doubt that the emission band of MS in the blue region (440 nm) results from the enol isomer (see Figure 1), which is produced by excited state intramolecular proton transfer (ESIPT) of the ketoB isomer (see Figure 1) in the first excited state. However, the source of the emission band of MS in the near-UV region is still debated. Initially, Weller1−3 proposed that, in the excited state of the ketoB isomer, there should be two minima: one is similar to the Franck–Condon (FC) structure, which we shall denote as ketoB*, the other is the enol isomer and is generated by ESIPT. Thus, the emission band of MS in the near-UV region would result from the ketoB* form. However, the energy barrier between the ketoB* and the enol forms in the first excited state predicted by Weller3 is extremely small: ≤0.12 kcal/mol. Later, theoretical studies using the CNDO/2 semiempirical method predicted an energy barrier of about 2.9 kcal/mol.4,5 Recently, Massaro and co-workers6 argued that their time-dependent density functional theory (TDDFT) studies confirm the existence of a double minimum in the excited state pathway along the O–H–O coordinate; however, the calculated energy barrier for the proton transfer is only about 0.02 kcal/mol. In addition, by studying the fluorescence and excitation spectra of isolated MS in a solid neon matrix at 4.2 K, Goodman and co-workers7 concluded that the ESIPT should be barrierless and that there was no clear spectroscopic evidence for an excited state double minimum proton transfer potential. The absence of a barrier for the ESIPT process is also supported by single-excitation CI (CIS) studies.8 Thus, it seems that there is no strong evidence supporting the existence of a double well in the first excited state of the compound and such a mechanism should be accepted only with reservations.

An alternative mechanism for the dual fluorescence of MS involves the existence of two molecular species in the ground state of MS. It was first postulated that there are two different structures in the ground state: ketoB and an open tautomer which does not contain a intramolecular hydrogen bond due to the 180° torsion of the hydroxyl group.9−11 The emission band of MS in the near-UV region was then postulated to be generated from the excited state of the open form of ketoB. However, this mechanism was not accepted widely; and recent DFT studies12 have demonstrated that the open form of ketoB

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lies at higher energy than the ketoB form by about 0.57 eV; thus, these two ground state species could not coexist at reasonable temperatures. Later studies proposed that the two different species in the ground state of MS are ketoA (see Figure 1) and ketoB, and it was postulated that the emission band of MS in the near-UV region results from the excited state of ketoA, where the ESIPT process cannot occur. Experimentally, in 1983, the presence of ketoA in the ground state was demonstrated by fluorescence emission IR
c and emission spectroscopy using a supersonic free-jet expansion.\n
However, the recent free-jet rotational spectra studies carried out by Melandri and co-workers did not detect the ketoA isomer in the ground state. Importantly, the recent DFT studies by Massaro et al. indicated that the energy barrier for the conversion reaction between ketoA and ketoB is about 15 kcal/mol; thus, the isomerization reaction ketoB \(\rightarrow\) ketoA is unlikely to occur at room temperature and only the ketoB isomer should exist.

Among the previous experimental studies, we note that the dual fluorescence of MS can apparently be observed in alcoholic solvents, i.e., methanol and ethanol, whereas it could not be observed in methycyclohexane and cyclohexane at room temperature. These indicate that the solvation effects play an important role in determining the dual fluorescence of MS. Especially the intermolecular hydrogen bonding (inter-HB) may play a significant role. However, solvent dependence has not gained enough attention in previous studies. A series of experimental and theoretical studies have demonstrated that the inter-HB plays an important role in determining the photophysical and photochemical properties of organic molecules (see ref 22 and references therein). In particular, the molecular fluorescence can be influenced by inter-HB between solute and alcoholic solvents in a number of ways. In addition, until now, the solvation effects have not been considered in the reported theoretical studies on MS. In the current work, a combined experimental and theoretical study was carried out to investigate the effects of solvation and inter-HB on the dual fluorescence of MS in a series of solvents, namely, methylcyclohexane (MCH), acetonitrile, dimethyl sulfoxide (DMSO), dimethylformamide (DMF), methanol, ethanol, propanol, and butanol. The solvents used here can be divided into two groups: the alcoholic solvents, which can form hydrogen bonds with MS, and the other solvents, which cannot form hydrogen bonds with MS.

Experimental Section

The solute MS (99%) was purchased from J&K Chemical and dissolved in solvents to a concentration of \(1 \times 10^{-3}\) M. The analytical reagent grade solvents were obtained from a commercial source and used as received. Steady-state absorption spectra were measured with a Lambda 35 UV/vis spectrometer (PerkinElmer Inc.). Steady-state fluorescence and time-resolved fluorescence decays were measured using a FluoroMax-4 Spectrofluorometer (Horiba-Jobin Yvon). Time-resolved fluorescence decays were recorded using the time-correlated single photon counting (TCSPC) method, and fitted to exponential functions with deconvolution of the measured instrument response function (IRF) using commercial software provided by Horiba Instruments.

Theoretical Methods

Gas Phase. First, the ketoB to ketoA isomerization reaction was investigated. The ground state geometries of isolated ketoA and ketoB isomers of MS were fully optimized without symmetry constraints using the DFT and RI-MP2 methods; then, frequency calculations at the same levels of theory were performed to confirm that each optimized structure was a real minimum (i.e., without imaginary vibrational frequencies). The geometry of the transition state of the ketoB to ketoA isomerization reaction (denoted as TS\(_{\text{ketoB-ketoA}}\)) was also optimized at the DFT and RI-MP2 levels and then ascertained by vibrational analysis to only have one imaginary frequency mode. To obtain a more accurate barrier height of the isomerization reaction, CCSD(T)(F12\(^\ast\)) single point energy calculations were carried out on the DFT and RI-MP2 optimized geometries. It should be noted that the energies of MP2-F12, SCS-MP2-F12, SOS-MP2-F12, and CCSD(F12\(^\ast\)) are also obtained during the CCSD(T)(F12\(^\ast\)) calculations.

Second, the inter-HB effects on the dual fluorescence of MS were investigated. The ketoB can form a hydrogen-bonded complex with methanol at two sites: with the hydroxyl group and with the carbonyl group. We denote these two hydrogen-bonded complexes as ketoB–methA and ketoB–methB, respectively. The ground and excited state geometries of ketoB–methA and ketoB–methB complexes were fully optimized with DFT and TD-DFT methods, respectively. Vibrational analyses were then performed at the optimized ground and excited state geometries with analytical and numerical methods, respectively, as implemented in the TURBOMOLE program. To validate the reliability of the TD-DFT results, the vertically excited singlet-state calculations...
were also carried out at the ADC(2)\textsuperscript{33,34} and RI-CC2\textsuperscript{35,36} levels.

All the calculations in the gas phase were carried out with the TURBOMOLE program.\textsuperscript{32} The PBE0 hybrid density functional was used throughout. The aug-cc-pVTZ basis set was used for DFT, TDDFT, RI-MP2, ADC(2), and RI-CC2 calculations, and the cc-pVTZ-F12 basis set was used for the F12 explicitly correlated coupled-cluster method CCSD(T)\textsuperscript{-}\textsuperscript{*}(F12\textsuperscript{*}) calculations. The fine quadrature grids m4 were employed in the DFT and TDDFT calculations, and convergence thresholds for the SCF were reset to be 10\textsuperscript{-7} (default settings are 10\textsuperscript{-6}) in all of the calculations.

**Solutions.** The ESIP reactions of ketoB in methycyclohexane (MCH; \( \varepsilon = 2.024 \)), acetonitrile (\( \varepsilon = 35.688 \)), dimethylformamide (DMF; \( \varepsilon = 37.219 \)), and dimethyl sulfoxide (DMSO; \( \varepsilon = 46.826 \)) were investigated using the TDDFT method. Solvation effects were included using the integral equation formalism\textsuperscript{37,38} (IEF) version of the polarizable continuum\textsuperscript{39,40} (PCM) model. The geometries of the ground and first excited states of MS in different solvents were optimized using the DFT and linear-response (LR) TDDFT methods, respectively. Vibrational analyses were performed to confirm that each optimized structure was a real minimum, i.e., without imaginary vibrational frequencies. Both LR and state-specific\textsuperscript{31,42} (SS) solvation models were used to compute the vertical excitation and emission energies of MS. Equilibrium solvation was assumed for geometry optimizations and emission energy calculations, whereas nonequilibrium solvation was used in vertical excitation energy calculations. Linearly interpolated internal coordinate (LIIC) pathways were constructed to follow the ESIP reaction of ketoB. The energy profiles were computed using the LR-TDDFT and SS-TDDFT methods with both equilibrium and nonequilibrium solvation models. All solution calculations were carried out using the Gaussian 09\textsuperscript{43} package. As is the case for the gas phase calculations, the PBE0 hybrid density functional was used throughout. The aug-cc-pVTZ basis set was adopted for geometry optimizations, vertical excitations, and emission energy calculations. Considering the computational cost, the somewhat smaller TZVP basis set was adopted for calculations of energy profiles along the LIIC pathways.

## RESULTS AND DISCUSSION

**Steady-State Absorption and Emission Spectra.** In Figure S1 (see the Supporting Information), we show the measured steady-state absorption spectra of MS in different solvents. From Figure S1 (Supporting Information), it can be seen that the absorption maxima of MS do not have a strong dependence on solvent (i.e., they varied from 305 to 308 nm in different solvents). Unlike the absorption spectra, the emission spectra of MS are significantly dependent on the solvent, as is shown in Figure 2. The dual fluorescence of MS can be observed in most of the solvents, with the exception of MCH. This is in accord with previous studies.\textsuperscript{2,9,10,13,21} In hydrogen-bonding systems (alcoholic solvents), the intensity of the near-UV band (around 350 nm) decreases with a decrease of the strength of inter-HB and the solvent polarity (methanol > ethanol > propanol > butanol), whereas the intensity of the blue band (around 450 nm) increases. In non-hydrogen-bonding systems, the intensity of the near-UV band increases with increasing solvent polarity (MCH < acetonitrile < DMF < DMSO), whereas the intensity of the blue band decreases. These findings clearly indicate that the relative intensities of the dual fluorescence of MS can be changed by inter-HB and solvent polarity. Further inspection of Figure 2 shows that the emission maxima of MS in alcoholic solvents are slightly larger than 350 nm, whereas in non-hydrogen-bonding systems the emission maxima of MS are slightly less than 350 nm. This difference may result from the inter-HB effects.

**Time-Resolved Fluorescence Decays.** We have measured the fluorescence decays of MS at 440 nm in different solvents and found that in all solvents the fitted fluorescence times are less than 200 ps. This is shorter than the time resolution of our instrument and indicates that the decay of the enol isomer of MS is fast. The measured time-resolved fluorescence decays of MS at 350 nm in different solvents from TCSPC data are shown in Figure S2 (see the Supporting Information), and the fitted fluorescence times are listed in Table 1. It is found that in alcoholic solvents the measured

![Table 1. Fitted Fluorescence Lifetime (in ns) of MS in Different Solvents from Time-Correlated Single Photon Counting (TCSPC) Data](#)

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Fitted Fluorescence Lifetime (in ns)</th>
</tr>
</thead>
<tbody>
<tr>
<td>methanol</td>
<td>0.526 (26%), 1.366 (61%), 9.331 (14%)</td>
</tr>
<tr>
<td>ethanol</td>
<td>0.428 (27%), 1.220 (70%), 8.612 (3%)</td>
</tr>
<tr>
<td>propanol</td>
<td>0.704 (45%), 2.150 (37%), 11.727 (18%)</td>
</tr>
<tr>
<td>butanol</td>
<td>0.732 (35%), 1.372 (59%), 15.900 (6%)</td>
</tr>
<tr>
<td>methylcyclohexane</td>
<td>0.809 (61%), 8.197 (39%)</td>
</tr>
<tr>
<td>acetonitrile</td>
<td>1.106 (94%), 6.531 (6%)</td>
</tr>
<tr>
<td>DMF</td>
<td>0.772 (97%), 11.23 (3%)</td>
</tr>
<tr>
<td>DMSO</td>
<td>0.736 (94%), 14.34 (6%)</td>
</tr>
</tbody>
</table>

The excitation wavelength is 295 nm.
fluorescence decays require three exponential functions, whereas in non-hydrogen-bonding solvents the measured fluorescence decays can be adequately described by biexponential functions. The different behavior in hydrogen-bonding and non-hydrogen-bonding solvents clearly indicates that inter-HB significantly affects the dual fluorescence of MS. According to our theoretical analysis, the fastest (less or slightly larger than 1 ns) decays observed in all of the solvents are attributable to our theoretical analysis, the fastest (less or slightly larger than 1 ns) decays observed in all of the solvents are attributable to the fluorescence lifetime of the ketoB, whereas decays of 1–2 ns are only observed in alcoholic solvents, and should result from the fluorescence lifetime of the hydrogen-bonding complex formed between the carbonyl group of MS and alcoholic solvents (denoted as ketoB–alcoholB, see Figure 3 for an example with methanol). The origin of the slowest decays (about 8–15 ns) observed in all solvents remains unclear for us. Here we assume that a small fraction of ketoA existed in the used MS sample and the slowest decays result from the fluorescence lifetime of ketoA. This assumption should be reasonable because, in a previous study, Orton et al. have shown that ketoA can be produced photochemically from ketoB, where the first triplet state of the compound is involved. This is further supported by Catalán in a recent study.19

**ketoB → ketoA Isomerization Reaction.** For ketoB, TS_ketoB2A, and ketoA, the optimized geometries in the gas phase using PBE0/aug-cc-pVTZ and RI-MP2/aug-cc-pVTZ are essentially identical to each other, with the computed bond lengths by these two methods differing by less than 0.01 Å (see Figure S3, Supporting Information). In Table 2, we list the computed energy barrier for the ketoB → ketoA isomerization reaction in the gas phase using DFT and RI-MP2 optimized geometries. Table 2 illustrates that, when the same method is applied on the DFT and RI-MP2 optimized TS geometries, the computed energy barriers are similar to each other. These data indicate that PBE0/aug-cc-pVTZ is sufficiently accurate to describe the ground state geometries of MS. Considering that CCSD(T)(F12*) is the most accurate method, the energy barrier of this reaction in the gas phase is predicted to be about 13 kcal/mol. We further calculate the energy barrier of this reaction in MCH, acetonitrile, DMF, and DMSO with the IEF-PCM model, and the computed values are about 12.8, 11.4, 11.4, and 11.3 kcal/mol, respectively. This indicates that the energy barrier of this reaction becomes lower in more polar solvents. Considering that the PBE0/aug-cc-pVTZ method would overestimate the energy barrier by about 1.5 kcal/mol when compared with the most accurate CCSD(T)(F12*) method, the energy barrier of this reaction in polar solvents can be estimated to be about 10 kcal/mol. This indicates that this reaction could not occur spontaneously, even in polar solvents, at room temperature and is in accord with the previous theoretical study by Massaro et al.22 However, taking into account that we could not guarantee that only the ketoB was prepared during the synthesis of MS, a small fraction of ketoA may also exist in the MS sample. This is why we attribute the slowest decays observed in all solvents to the fluorescence lifetime of ketoA. In addition, it should be noted that this energy barrier (~10 kcal/mol) can be overcome at high temperature, which explains why the intensity of the near-UV band of MS in cyclohexane rises with temperature increases.14

**Inter-HB Effects in Alcoholic Solvents.** We then investigated the effects of inter-HB on the dual fluorescence of MS. We used methanol as the example and first optimized the ground state geometries of ketoB–methA and ketoB–methB complexes. When we performed frequency calculations on the optimized ground state geometries of ketoB–methA and ketoB–methB complexes, we obtained two very small imaginary frequencies, 5.69i and 0.63i for ketoB–methB, respectively. Both of these correspond to the stretching vibration of the intermolecular hydrogen bond, and

<table>
<thead>
<tr>
<th>Method</th>
<th>ketoA</th>
<th>ketoB</th>
<th>TS_ketoB2A</th>
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<th>ketoA</th>
<th>ketoB</th>
</tr>
</thead>
<tbody>
<tr>
<td>PBE0</td>
<td>4.14</td>
<td>14.48</td>
<td>4.13</td>
<td>14.48</td>
<td>3.23</td>
<td>12.34</td>
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<tr>
<td>RIMP2</td>
<td>3.29</td>
<td>12.47</td>
<td>3.05</td>
<td>11.66</td>
<td>3.35</td>
<td>12.52</td>
</tr>
<tr>
<td>MP2-F12</td>
<td>3.05</td>
<td>11.66</td>
<td>2.93</td>
<td>11.26</td>
<td>3.16</td>
<td>11.81</td>
</tr>
<tr>
<td>SCS-MP2-F12</td>
<td>2.93</td>
<td>11.26</td>
<td>3.26</td>
<td>12.46</td>
<td>3.07</td>
<td>11.45</td>
</tr>
<tr>
<td>SOS-MP2-F12</td>
<td>3.26</td>
<td>12.46</td>
<td>3.34</td>
<td>12.91</td>
<td>3.40</td>
<td>13.02</td>
</tr>
<tr>
<td>CCSD(T)(F12*)</td>
<td>3.26</td>
<td>12.46</td>
<td>3.34</td>
<td>12.91</td>
<td>3.40</td>
<td>13.02</td>
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</tr>
</thead>
<tbody>
<tr>
<td>RI-MP2</td>
<td>0.00</td>
<td>11.41</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>aug-cc-pVTZ Optimized Geometries</td>
<td>0.00</td>
<td>11.41</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>PBE0/aug-cc-pVTZ Optimized Geometries</td>
<td>0.00</td>
<td>11.41</td>
<td>0.00</td>
<td>0.00</td>
</tr>
</tbody>
</table>

*For each method, the energy of ketoB was set to zero.*
we were unable to remove them during our calculations even if we tightened the numerical convergence thresholds. Irrespective of the precise numerical value, these indicate that both of these two intermolecular hydrogen bonds are weak in the ground state. For ketoB and ketoB−methA, when we optimized the first excited state (S₁) geometries starting from the ground state (S₀) geometries, we directly obtained the corresponding enol form, indicating that the ESPT processes of ketoB and ketoB−methA are either barrierless or have an insignificant barrier. Whereas for ketoB−methB, using either the S₀ geometry or the corresponding enol form as the initial structure, we never observed optimization to the enol form; this supports the hypothesis that the ESPT process of ketoB−methB is precluded by inter-HB. Inspecting the computed bond lengths shown in Figure 3, it can be seen that the intermolecular hydrogen bonds of ketoB−methA and ketoB−methB are both shortened, and presumably strengthened, in the S₁ state. The strengthening of the intermolecular hydrogen bond will facilitate the ESPT process for ketoB−methA and hinder the ESPT process for ketoB−methB. It should be emphasized that all of the computed vibrational frequencies at the S₁ state geometries of ketoB−methA and ketoB−methB are positive.

Thus, in alcoholic solvents, the near-UV band of MS will result from ketoB-alcoholB-S₁, whereas the blue band will result from enol-S₁ and enol-alcoholA-S₁. Changing solvents from methanol to butanol, the strength of inter-HB between MS and the alcoholic solvent will decrease. Thus, the intensity of the near-UV band will decrease and the blue band will increase. This is in accord with our experimental observations. Our further theoretical studies will confirm that ketoB* will also contribute to the emission band in the near-UV.

In Figure 3, we also show the computed excitation and emission energies of ketoB, ketoB−methA, and ketoB−methB using the TD-PBE0, ADC(2),33,34 and RI-CC235,36 methods. From Figure 3, it can be seen that all the computed excitation and emission energies by these three methods are in good agreement with the experimental values; the best agreement was obtained by RI-CC2 methods, while the computed emission energies by ADC(2) are slightly underestimated.

ESPT Reactions of ketoB in Polar Solvents. As described previously, our theoretical studies in the gas phase could not locate the ketoB* isomer in the first excited state, indicating that the ESPT of ketoB in the gas phase should be essentially barrierless. We then tried to optimize the first excited state geometries of ketoB* in MCH, acetonitrile, DMF, and DMSO with the IEF-PCM solvation model; instead, we still directly obtained the equilibrium geometries of the corresponding enol form. This seems to indicate that the ESPT of ketoB in polar solvents will still be barrierless and cannot be used to explain why the relative intensities of the dual fluorescence of MS are changed from MCH to DMSO. It should be noted that the optimization of the first excited state geometries of MS was performed within the LR framework with equilibrium solvation. However, in consideration of recent studies1,42 that have pointed out that in polar solvents the SS approach will provide more accurate results than LR, additional SS calculations were performed. In Table S1 (Supporting Information), we show the computed vertical excitation (ketoB) and emission energies (from enol isomer) of MS in different solvents with LR and SS solvation at the PBE0/aug-cc-pVTZ level. It can be seen that the computed excitation and emission energies using the SS approach are slightly blue-shifted when compared with those of the LR approach.

To further check whether a double well exists in the ESPT pathways of ketoB and whether ketoB* can contribute to the near-UV emission band, we constructed LIIC pathways between the optimized ground state geometries of the ketoB isomer and the first excited state geometries of the enol isomer and performed single point energy calculations along the constructed LIIC pathways. Considering the computational cost, we used the TZVP basis set for calculations of energy profiles along the LIIC pathways. Before doing this, we confirmed that the calculated results with the TZVP basis set are sufficiently similar to those using the aug-cc-pVTZ basis set. Representative optimized geometries of MS in DMF by PBE0/aug-cc-pVTZ and PBE0/TZVP are shown in Figure S4 (Supporting Information). It can be seen that the computed bond lengths by these two basis sets are essentially identical.

In Figure 4, we show the computed energy profiles along the constructed LIIC pathways with linear-response (LR, top),
state-specific nonequilibrium (SS-NonEq, middle), and equilibrium (SS-Eq, bottom) solvation. From Figure 4, the following is revealed: (i) In the nonpolar solvent MCH, the computed LIIC pathways (by all three methods) can be regarded as barrierless. This provides theoretical support that the ESIPT of MS in MCH is barrierless and is in accord with the experimental result that only a very small shoulder around 350 nm was observed in MCH. (ii) In the polar solvents acetonitrile, DMF, and DMSO, an obvious barrier is observed along the computed LIIC pathways. Within the LR framework, the estimated barriers for ESIPT reaction of ketoB in these three solvents are less than 0.5 kcal/mol. This is very small, and in retrospect, it is not surprising that we could not locate the equilibrium geometries of ketoB* in these three solvents. Within the SS framework, the barrier increased to about 1.3 kcal/mol. And importantly, the barrier for the back proton transfer from the enol isomer to ketoB* decreased from about 6.8 to 4.8 kcal/mol. Thus, it should be expected that an equilibrium will be formed between ketoB* and the enol isomer in acetonitrile, DMF, and DMSO and that ketoB* will contribute to the near-UV emission band. (iii) Using either LR or SS approaches, the computed LIIC curves for acetonitrile, DMF, and DMSO are essentially identical, indicating that our calculated results cannot further distinguish the experimentally observed differences of emission spectra of MS in these three solvents. This may be due to an approximation made in the IEF-PCM model (e.g., loss of solvent dispersion) that could affect the barrier height.

**CONCLUSIONS**

In summary, we present a combined experimental and theoretical study on the dual fluorescence of MS in a number of solvents. For the first time, we point out that inter-HB (i.e., intermolecular hydrogen bonding) plays a significant role in the dual fluorescence of MS in alcoholic solvents. The ESIPT process of ketoB will be precluded when the intermolecular hydrogen bond is formed between the carbonyl group of ketoB and alcoholic solvents, which is the source of the emission band in the near-UV region. In addition, our theoretical studies indicated that the barrier height between ketoB* and an enol isomer of MS in the excited state is solvent-dependent. On the basis of these findings, a new mechanism for the dual fluorescence of MS in solvents was proposed, as illustrated in Figures 3 and 5. The following should be emphasized: (1) The barrier height for ESIPT reaction of ketoB in the gas phase and in nonpolar solvents is very small; thus, dual fluorescence of MS under these conditions is not observed. The observed weak shoulder around 350 nm in the gas phase and in nonpolar solvents is assumed to result from the ketoA isomer, because a small fraction of ketoA is likely to exist in the MS sample. (2) In alcoholic solvents, ketoB* can also contribute to the near-UV band; however, inter-HB plays a more important role than ketoB*. (3) The energy barrier for the ketoB → ketoA isomerization reaction can be overcome at high temperatures; thus, the intensity of the near-UV band will increase with increasing temperature, as a previous experiment predicted.

**ASSOCIATED CONTENT**

Supporting Information

The following materials are provided: full citation of ref 43; computed vertical excitation (ketoB) and emission energies (from enol, in nm) of MS in different solvents with LR and SS solvation at the PBE0/aug-cc-pVTZ level; measured steady-state absorbance spectra of MS in different solvents; measured time-resolved fluorescence decays of MS in different solvents from time-correlated single photon counting (TCSPC) data; and all optimized geometric coordinates. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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