The mechanisms of a bifunctional fluorescent probe for detecting fluoride and sulfite based on excited-state intramolecular proton transfer and intramolecular charge transfer

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ABSTRACT

The mechanisms of 2-(Benzo[d]thiazol-2-yl)phenol-based bifunctional probe (HBT-FS) for detecting fluoride (F^-) and sulfite (SO_3^{2-}) based on excited-state intramolecular proton transfer (ESIPT) and intramolecular charge transfer (ICT) have been theoretically studied. Laplacian bond order of HBT-FS indicates that the F^- ion cleaves the Si-O bond and then forms Compound 2 possessing a six-membered ring with a hydrogen bond. Potential energy curves and dynamic simulations confirm that ESIPT in Compound 2 occurs along with this hydrogen bond and forms a keto structure with an emission at 623 nm, which agrees with the observed experimental value (634 nm) after adding F^- . Therefore, the fluorescence red-shift (from 498 to 634 nm) of HBT-FS observed in experiment after adding F^- is caused by ESIPT. The SO_3^{2-} ion is added to the C_5 site of HBT-FS, which is confirmed by orbital-weighted dual descriptor, and then forms Compound 3 with fluorescence located at 404 nm. The experimentally measured fluorescence at 371 nm after adding SO_3^{2-} is assigned to Compound 3. Charge transfer analyses indicate that the ICT extent of Compound 3 is relatively weak compared with that of HBT-FS because of the destruction of the conjugated structure by the addition reaction of SO_3^{2-} , which induces the blue-shift of the fluorescence of HBT-FS from 498 to 371 nm. The different fluorescence responses make HBT-FS a fluorescent probe to discriminatorily detect F^- and SO_3^{2-} .

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I. INTRODUCTION

Fluorescent probes have received increasing attention due to their high sensitivity, good selectivity, reliability, noninvasive, and real time detection.^{1–6} A variety of fluorescent probes have been developed to detect cations, anions, and biomolecules *in vitro* and *in vivo*. The different detection mechanisms have been revealed and the common detection strategy is to observe the changes in fluorescence intensity or fluorescence wavelength.^{7–16} Therefore, it is key to design a probe with the fluorescence signal showing obvious change after adding the analyte. Organic molecules with excited-state intramolecular proton transfer (ESIPT) process often exhibit different photophysical properties before and after proton transfer because ESIPT induces a tautomerization process, the change of geometric structure from enol to keto form induced by the transfer of protons along with hydrogen bonds usually causes the

large Stokes shift in fluorescent, which has been excessively studied. $^{17-28}$ This unique photophysical property makes compounds with ESIPT ideal materials for the design of fluorescent probes with many potential applications, such as luminescent materials, photostabilizers, laser dyes, and so on. $^{29-36}$

As one of the benzothiazole derivatives, 2-(Benzo[d]thiazol-2yl)phenol (HBT) exhibits a typical ESIPT process and is recognized as an ideal fluorophore to design the ratiometric fluorescent probes. So far, many probes for different analytes have been designed and synthesized based on a core of HBT. Wu *et al.* used HBT as fluorophore to synthesize two ratiometric probes (named HBT-ratio-F1 and HBTratio-F2) for detecting fluoride ions.³⁷ Wang and his co-workers constructed a novel HBT-based near-infrared fluorescent probe for the detection of bisulfite.³⁸ Yang *et al.* developed a rhodol derivative that contains HBT as a ratiometric fluorescent probe for sulfite.³⁹ These probes have only one recognition group, so they can detect one kind of analyte at a time. However, there is more than one species in the real sample, so it is necessary to develop a multifunctional probe that can distinguish two or more analytes at the same time. Lately, a HBTbased bifunctional ratiometric fluorescent probe 2-(4-(benzo[d]thiazol-2-yl)-3-((tertbutyldimethylsilyl)oxy)benzylidene)malononitrile (HBT-FS) has been designed and synthesized by Song and his coworkers for the discriminative detection of fluoride (F⁻) and sulfite (SO₃²⁻).⁴⁰ HBT-FS has two sensing groups: (1) tert-butyldimethylsilyl ether moiety is sensitive to F⁻ and (2) C-C double bond is sensitive to SO_3^{2-} . The spectral responses of HBT-FS to F⁻ and SO_3^{2-} have been measured in the titration experiments, showing that F^- and SO_3^{2-} induced the red-shift and blue-shift of the fluorescence of HBT-FS, respectively. Song and his co-workers proposed that HBT-FS discriminatorily detect F⁻ and SO₃²⁻ by the combination of the ESIPT and intramolecular charge transfer (ICT) mechanisms. However, the proposed mechanisms lack theoretical verification. The ESIPT process needs to be further theoretically determined because the unique dual fluorescence feature of ESIPT was not observed in the experiment. In addition, the information of ICT cannot be provided through the experiment and needs to be analyzed by theory.

In this work, the theoretical calculations by density functional theory (DFT) and time-dependent density functional theory (TD-DFT) are conducted to investigate photophysical properties before and after the addition of F⁻ and SO₃²⁻ and reveal the detection mechanisms of HBT-FS to F⁻ and SO₃²⁻. Laplacian bond order (LBO) and orbital-weighted dual descriptor isosurface are calculated to determine the reaction sites of F⁻ and SO₃²⁻. The possible geometric configurations of HBT-FS and the products (Compound 2 and Compound 3) in the ground (S₀) state and the first excited (S₁) state have been optimized, and the absorption and emission spectra are simulated based on these optimized structures. Moreover, the scanned potential energy curves and dynamic simulations of Compound 2 are performed to investigate the ESIPT reaction kinetics. The frontier molecular orbitals (FMOs) and the isosurface of C₊ and C₋ functions are analyzed to explore the ICT properties.

II. COMPUTATIONAL DETAILS

In this work, the structures of HBT-FS and its products in the S₀ and S1 states are optimized with the DFT and TDDFT methods, respectively. In the optimization process, the structures are not constrained. The transition state is searched with the transition state theory. Frequency analyses confirm that these optimized configurations have no imaginary mode and the transition state has only one imaginary frequency, which is further ensured by the intrinsic reaction coordinate (IRC) calculation. For the above calculations, after testing a large number of functionals (see Table S1), the mPW1PW91 functional combined with TZVP basis set is adopted because of the consistency with the experimental result.^{41,42} Considering the experimental environment, acetonitrile (ACN) is chosen as the solvent by using the integral equation formalism variant of the polarizable continuum model (IEFPCM).^{43,44} The absorption and emission spectra are calculated based on the optimized structures. All calculations in this work are carried out by Gaussian 16 package and dynamic simulations are performed by using Newton-X interfaced with Gaussian.^{45,46} LBO and orbital-weighted dual descriptor as well as the isosurface of C₊ and C₋ functions are analyzed by Multiwfn based on the outputs of Gaussian.⁴

III. RESULTS AND DISCUSSION

A. Geometric structures

In order to investigate the sensing progress, the geometries of the fluorescent probe HBT-FS in the S₀ and S₁ states have been optimized at the mPW1PW91/TZVP theoretical level. As shown in Fig. 1, HBT-FS is based on a core of 2-(benzo[d]thiazol-2-yl)phenol (HBT) and has two sensing groups, which are the tert-butyldimethylsilyl moiety and the dicyanovinyl group, respectively. The tert-butyldimethylsilyl moiety for detecting F⁻ masks the phenolic hydroxyl group into the ether group, which inhibits the proton transfer process. The dicyanovinyl group for recognizing SO₃²⁻ is attached to the meta position of the phenolic hydroxyl group in HBT and acted as an electron-withdrawing group. It can be seen from Fig. 1 that the benzothiophene moiety in HBT-FS is not coplanar with the benzene ring, and the



FIG. 1. Optimized structures of the fluorescent probe HBT-FS and the corresponding reaction product Compound 2 and Compound 3 at the mPW1PW91/TZVP theoretical level. Blue: N; Light blue: H; Gray: C; Yellow: S; Red: O; Fuchsia: Si.

dihedral angles $\delta_{(C1-C2-C3-S)}$ in the S₀ and S₁ states are 41.97° and -14.65° , respectively. The change of the dihedral angle $\delta_{(C1-C2-C3-S)}$ from the S₀ state to the S₁ state indicates that the benzothiophene moiety is twisted and is more coplanar with the benzene ring in the S1 state. The bond length of C4-C5 double bond in the dicyanovinyl group changes from 1.358 Å in the S_0 state to 1.400 Å in the S_1 state, which is extended by 0.042 Å. After adding F⁻, the tertbutyldimethylsilyl ether bond is cleaved to form Compound 2, which is also shown in Fig. 1. In Compound 2, the phenolic hydroxyl group is restored and forms an intramolecular hydrogen bond O-H…N with the adjacent nitrogen atom. The bond lengths of O-H and H…N in the S₀ state are 0.995 Å and 1.691 Å, respectively. Upon photoexcitation, the bond lengths of O-H and H ... N changes to 1.008 and 1.644 Å, respectively. In addition, the bond angle of θ (O-H…N) is increased from 147.6° the S0 state to 148.8° in the S1 state. Based on the lengthening of the O-H bond length and the shortening of the H…N bond length as well as the increase of the bond angle of θ (O-H···N), it can be confirmed that the intramolecular hydrogen bond O-H…N is strengthened in the S₁ state, which will provide a driving force for proton transfer. The dihedral angles $\delta_{(C1-C2-C3-S)}$ in the S₀ and S_1 states are both 0° , indicating that Compound 2 has a planar structure. The C₄-C₅ double bond lengths of Compound 2 in the S₀ and S1 states are the same as those of HBT-FS, respectively, which are both not changed. For Compound 3 displayed in Fig. 1, it is the product formed after the addition of SO₃²⁻. The dihedral angle $\delta_{(C1-C2-C3-S)}$ in Compound 3 changes from -44.45° in the S₀ state to 3.06° in the S₁ state, which demonstrates that the mainframe HBT is more planar in the S_1 state. However, the C_4 - C_5 bond length becomes 1.561 Å in the S_0 state, which is close to the length of C-C single bond. Thus, it can be confirmed that the C4-C5 double bond of the dicyanovinyl group is broken and that the conjugate system is interrupted by SO_3^{2-} .

B. Reactive site

Laplacian bond order (LBO) is a newly defined bond order based on a scaled integral of the Laplacian of electron density negative parts in fuzzy overlap space, which can better identify bonding strength because of the direct correlation with the bond dissociation energy.⁴⁸ LBO for all bonds of HBT-FS has been calculated by Multiwfn to determine the cleavage site of F⁻. As shown in Fig. 2(a), the calculated LBO of Si-O bond (0.198) is significantly smaller than that of other bonds, indicating that the bonding strength of Si-O bond is relatively weak. Therefore, the Si-O bond is a favorable cleavage site. In addition, the transition state and the Gibbs free energy barrier of the cleavage reaction are calculated. The searched transition state is verified by IRC (shown in Fig. S1) to be correct. The Gibbs free energy barrier of this reaction is 9.15 kcal/mol. This relatively small energy barrier further indicates that the reaction is prone to occur. For the addition reaction of SO₃²⁻, the orbital-weighted dual descriptor constructed from Fukui functions is calculated to predict the reactive site.⁴⁹ The green and blue isosurfaces shown in Fig. 2(b) represent nucleophilic and electrophilic regions, respectively. In general, a site with a large green or blue isosurface has remarkable nucleophilicity or electrophilicity. It is noted that the green isosurfaces distributed on the C4 and C5 atoms of C4-C5 double bond are relatively large, confirming that the C4 and C5 atoms are susceptible to undergo nucleophilic attack. In order to quantitatively assess nucleophilicity of the C4 and C5 sites, the condensed local nucleophilicity indices are calculated based on conceptual density functional, which are 0.0218 and 0.0748, respectively. Therefore, the C_5 site has high nucleophilicity and SO_3^{2-} should be added to this site. The transition state is searched and found at the position where the C4-C5 double bond is broken and the C-S bond is formed, which is further confirmed by IRC calculations (shown in Fig. S2).

C. Proton transfer in Compound 2

In Compound 2, the six-membered hydrogen bond ring formed by the phenolic hydroxyl group and the adjacent nitrogen atom provides a possibility for the proton transfer. In order to verify whether proton transfer can occur, the potential energy curves of the S_0 and S_1 states are scanned as a function of the O-H bond length, which can provide the change of energy with bond length. As seen from Fig. 3, the energy of the S_0 state increases with the extension of the O-H bond length, indicating that the proton transfer process in the S_0 state is unlikely to occur. However, there is an energy barrier of 1.99 kcal/ mol between the enol and keto form in the S_1 state, which is quite small and can be easily overcome. Thus, the proton transfer process of Compound 2 occurs in the S_1 state and then forms a stable keto structure at the O-H bond length of 1.808 Å.

In order to reveal more details of proton transfer process, the dynamic simulations of Compound 2 are performed by using Newton-X interfaced with Gaussian program. The initial conditions for each trajectory are generated by a sampling procedure using a harmonic-oscillator Wigner distribution for each normal mode.



FIG. 2. Laplacian bond order (LBO) for all bonds (a) and orbital-weighted dual descriptor isosurface of HBT-FS (b)



FIG. 3. The calculated potential energy curves of Compound 2 in the S₀ and S₁ states at the MPW1PW91/TZVP theoretical level.

Thirty-two trajectories as a representative set are simulated with a time step of 1 fs under an NVT ensemble at 300 K. The simulated time range is set to 300 fs, which is long enough to cover an ultrafast proton transfer process. In these classical dynamics simulations, results such as state character, energies, and internal coordinates can be described by statistical analysis. The time evolutions of energies and bond lengths are shown in Figs. 4(a) and 4(b). As seen from Fig. 4(a), no surface hopping between the S₀ and S₁ states exists, and the current state is located at the S1 state, indicating that proton transfer will occur in the S₁ state. These analyses' results are consistent with that of the potential energy curve analysis. The proton transfer time is defined as the average time in which the distances of the O-H and N-H bonds become equal, that is, the time at the intersection in Fig. 4(b). It can be seen from Fig. 4(b) that the intersection between the two bonds of O-H and N-H indicates proton transfer time constant at 155 fs, which further confirms the occurrence of ESIPT.

D. Electronic spectra

The titration experiment shows that upon the addition of F^- , the absorption peak at approximately 385 nm decreases gradually

accompanying the appearance of two new peaks (approximately 400 and 350 nm). However, after the addition of SO32-, only one absorption peak at approximately 300 nm is found. In order to investigate the attribution of these absorption peaks, the six low-lying absorbing transitions of HBT-FS, Compound 2, and Compound 3 are calculated based on the optimized structures of the S_0 state at the mPW1PW91/ TZVP theoretical level. Only the singlet transitions with wavelengths >300 nm are listed in Table I and the calculated absorption spectra are displayed in Fig. 5. As seen from Table I, for HBT-FS, the absorption peak corresponding to the first singlet transition $(S_0 \rightarrow S_1)$ is at 392 nm with the oscillator strength of 0.6358, which is in accord with the experimental value (385 nm). For Compound 2, there are two permitted singlet transitions ($S_0 \rightarrow S_1$ and $S_0 \rightarrow S_3$), which are at 419 and 352 nm, respectively. The calculated absorption peaks of Compound 2 coincide with the two peaks (400 and 350 nm) appearing after the addition of F⁻, which further confirms that Compound 2 is the product. The absorption peak of Compound 3 is calculated to be at 307 nm, which is consisted with the experimental data (300 nm). Therefore, the newly formed absorption peak after the addition of SO_3^{2-} is attributed to Compound 3.



TABLE I. The calculated electronic excitation energies (nm), corresponding oscillator strengths, and the corresponding compositions of the low-lying singlet excited states for HBT-FS, Compound 2, and Compound 3.

	Transition	λ (nm)	f^{a}	Composition ^b	CI (%) ^c
HBT-FS	$S_0 \rightarrow S_1$	392	0.6358	$H {\rightarrow} L$	95.55%
	$S_0 \rightarrow S_2$	363	0.0066	$H-1 \rightarrow L$	98.48%
	$S_0 \rightarrow S_3$	345	0.2286	$H-2 \rightarrow L$	71.09%
	$S_0 \rightarrow S_4$	335	0.0111	$H-3 \rightarrow L$	73.23%
Compound 2	$S_0 \rightarrow S_1$	419	0.7075	$H {\rightarrow} L$	96.42%
	$S_0 \rightarrow S_2$	359	0.0364	$H-1 \rightarrow L$	84.99%
	$S_0 \rightarrow S_3$	352	0.4659	$H-2 \rightarrow L$	81.57%
Compound 3	$S_0 {\rightarrow} S_1$	307	0.3983	$H {\rightarrow} L$	68.62%

^aOscillator strength.

 $^{\mathrm{b}}\mathrm{H},$ HOMO (highest occupied molecular orbital) and L, LUMO (lowest unoccupied molecular orbital).

°CI, Composition index.

The fluorescence peak changed with incremental addition of Fand SO_3^{2-} to the solution of HBT-FS. The fluorescence at 498 nm gradually declined with the increase in F⁻ and a new emission peak at 634 nm appeared simultaneously. For the addition of SO_3^{2-} , the emission peak shifted from 498 to 371 nm. To study the fluorescence properties of HBT-FS, Compound 2, and Compound 3, the emission energies are calculated based on the optimized structures in the S₁ state. The corresponding calculation results are listed in Table II and the spectral curves are shown in Fig. 5. The calculated emission peak of HBT-FS is at 518 nm, which is in accordance with the experimental value (498 nm). For Compound 2, the $S_1 \rightarrow S_0$ emission energies of the enol and keto structures have been calculated, which are at 511 and 623 nm, respectively. The emission peak of the keto structure agrees with the emission peak at 634 nm appearing after the addition of F⁻. Therefore, the fluorescence peak at 634 nm measured in the experiment is emitted from the keto structure rather than the enol structure, which has a red-shift of 105 nm compared to that of HBT-FS. As for Compound 3, the calculated emission peak is at 404 nm, which is close to the emission peak (371 nm) appearing after the addition of SO_3^{2-} . Thus, the experimentally measured fluorescence of 371 nm is assigned to Compound 3, which has a blue shift of $114\,\mathrm{nm}$ compared to that of HBT-FS.

E. Charge transfer

In order to study the properties of charge transfer and explain the spectral shifts induced by F^- and SO_3^{2-} , the frontier molecular orbitals involved in the absorption and emission of HBT-FS, Compound 2, and Compound 3 are shown in Fig. 6. It can be seen from Table I that the first singlet transitions $(S_0 \rightarrow S_1)$ for all molecules involve only the electronic transitions from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO), which are all $\pi\pi^*$ -type transitions. As seen from Fig. 6, for HOMO of HBT-FS, the electron density is mainly localized on the frame molecule HBT. While for LUMO, it is mainly distributed on the benzene ring and dicyanovinyl moiety. Therefore, charge transfer occurs in HBT-FS upon photo-excitation. For Compound 2, the charge transfer characteristic of the $S_0 \rightarrow S_1$ transition is similar to that of HBT-FS and the second permitted singlet transition $(S_0 \rightarrow S_3)$ is dominated by the transition from HOMO-2 to LUMO, which also has a $\pi\pi^*$ feature. For Compound 3, the first singlet transition $(S_0 \rightarrow S_1)$ corresponding to the transition from HOMO to LUMO involves a charge transition process from HBT to dicyanovinyl moiety. As for the emission of HBT-FS, Compound 2, and Compound 3, the $S_1 \rightarrow S_0$ transitions are all corresponding to the electronic falling from LUMO to HOMO. It can be noted that the electron density on dicyanovinyl moiety in HBT-FS and Compound 2 decreases and ICT in Compound 3 mainly occurs on the frame molecule HBT due to the destruction of the conjugated structure by the addition reaction of SO_3^{2-} . For Compound 2, it can be noted that the energy gap of keto structure (2.66 eV) from LUMO to HOMO is smaller than that of enol structure (3.55 eV), indicating that keto form structure will emit longwavelength fluorescence. Thus, the red-shift of fluorescence after adding F^- is caused by ESIPT. For Compound 3, the energy gap (3.82 eV) from LUMO to HOMO increases compared to that of HBT-FS (3.02 eV), which will emit relatively short-wavelength fluorescence.

In order to compare the ICT characteristics between the S_0 and S_1 states quantitatively, the electron density differences in the S_0 and S_1 structures are calculated for HBT-FS, Compound 2, and Compound 3. Figure 7(a) shows the electron density difference in the S_0 structure



FIG. 5. The calculated absorption and fluorescence emission spectra of HBT-FS, Compound 2, and Compound 3 at the mPW1PW91/TZVP theoretical level

	Form	Transition	λ (nm)	fª	Composition ^b	CI (%) ^c	Exp. (nm) ^d
HBT-FS		$S_1 \rightarrow S_0$	518	1.1852	$L {\rightarrow} H$	99.07%	498
Compound 2	enol	$S_1 \rightarrow S_0$	511	1.1569	$L \rightarrow H$	98.97%	
	keto	$S_1 \rightarrow S_0$	623	0.3117	$L \rightarrow H$	99.83%	634
Compound 3		$S_1 \rightarrow S_0$	404	1.1071	$L {\rightarrow} H$	98.51%	371

TABLE II. The calculated fluorescence emission band in ACN at the mPW1PW91/TZVP theoretical level and the experimental value.

^aOscillator strength.

^bL, LUMO (lowest unoccupied molecular orbital) and H, HOMO (highest occupied molecular orbital).

^cCI, Composition index.

^dThe experimental value of the fluorescence peak.

during the electron excitation. The green and blue regions correspond to positive and negative regions, respectively, which represent the increase and decrease in electron density in the electron excitation process. It can be noted that the increase in electron density is mainly in dicyanovinyl moiety, which is consistent with the results of FMOs analysis. In order to visualize the characteristics of charge transfer more intuitively, the isosurfaces C+ and C_ functions are shown in Fig. 7(b). C_+ and C_- functions proposed by Bahers *et al.* represent two centroids of charges associated with the positive and negative density regions, respectively, which make the direction of electron transfer clearly visible.⁵⁰ In addition, the distance between the barycenters of C₊ and C₋ can be used to measure the charge-transfer length to evaluate the charge-transfer degree. In general, the longer the chargetransfer length, the greater the charge-transfer degree. It can be seen from Fig. 7(b) that the charge-transfer lengths between the barycenters of C₊ and C₋ in HBT-FS, Compound 2, and Compound 3 are 4.514, 3.968, and 1.072 Å, respectively. Therefore, compared to HBT-FS and Compound 2, Compound 3 has the smaller charge transfer distance, indicating that Compound 3 has a smaller extent of charge transfer characteristic corresponding to the $S_0 \rightarrow S_1$ transition. In addition, the

dipole moment variations from the S_0 state to the S_1 state for HBT-FS and Compound 2, Compound 3 are 11.30 D, 14.75 D, and 3.19 D, respectively. The insignificant dipole moment variation of Compound 3 further illustrates a weak ICT characteristic in Compound 3.

Figures 7(c) and 7(d) show the electron density differences and the isosurface of C₊ and C₋ functions based on the S₁ structures in the electron de-excitation process, respectively. It can be noted that the charge-transfer lengths for all molecules vary as the structures transfer from the S₀ state to the S₁ state. The ICT distances corresponding to the $S_1 \rightarrow S_0$ transition of HBT-FS, Compound 2, and Compound 3 become 3.991, 3.956, and 1.301 Å, respectively. The ICT distance in Compound 3 is still the smaller one compared to that in HBT-FS and Compound 2, confirming a smaller ICT extent. Thus, the addition reaction of SO32- weakens the ICT extent, which leads to the blue-shift (from 498 to 371 nm) of the fluorescence of HBT-FS. In addition, it can be seen that the ICT distances of HBT-FS and Compound 3 change relatively obviously compared to that of Compound 2. This is because the molecular structures of HBT-FS and Compound 3 undergo rearrangement, which has been confirmed by the changes of dihedral angles $\delta_{(C1-C2-C3-S)}$ from the S₀ state to the S₁ state.



FIG. 6. Frontier molecular orbitals involved in the vertical excitation and emission of HBT-FS, Compound 2, and Compound 3.



FIG. 7. The electron density difference between the S_0 and S_1 states in the S_0 structure (a) and in the S_1 structure (c). The isosurface of C_+ (green) and C_- (blue) functions as well as the charge-transfer distances for HBT-FS, Compound 2, and Compound 3 in the S_0 structure (b) and in the S_1 structure (d).

F. Detection mechanisms

According to the previous spectral measurements and the current theoretical calculations, the fluorescent probe HBT-FS exhibits different fluorescence responses to F⁻ and SO₃²⁻. Based on the correlation analyses, the detection mechanisms of HBT-FS for F^- and SO_3^{2-} can be plotted as in Fig. 8. HBT-FS with the tertbutyldimethylsilyl moiety and the dicyanovinyl group as sensing groups shows an emission peak at 498 nm. The addition of Fcleaves the tert-butyldimethylsilyl ether bond in HBT-FS to form Compound 2 with a six-membered hydrogen bond ring. Upon photo-excitation, an ESIPT process in Compound 2 occurs along the hydrogen bond to form a keto structure with an emission at 623 nm, which is red-shifted compared to the emission peak of HBT-FS. For the addition of SO_3^{2-} , it will be added to the C₅ site of the C₄-C₅ double bond in HBT-FS to form a Compound 3 with an emission at 371 nm. The addition reaction of SO_3^{2-} breaks the conjugate structure of HBT-FS and weakens the intramolecular charge transition, thereby inducing the fluorescence blue-shift of HBT-FS from 498 to 371 nm. Based on the different fluorescence behaviors induced by the addition of F^- and SO_3^{2-} , HBT-FS can act as a fluorescent probe to discriminatorily detect F⁻ and SO_3^{2-} .

IV. CONCLUSIONS

In this work, the DFT and TDDFT calculations have been performed to investigate the detection mechanisms of 2-(benzo[d]thiazol-2-yl)phenol-based bifunctional probe (HBT-FS) for F⁻ and SO₃²⁻. LBO confirms that Si-O bond in HBT-FS is easily cleaved by F⁻ due to a smaller LBO (0.198) and then forms Compound 2 with a sixmembered hydrogen bond ring. The constructed potential energy curves and dynamic simulations demonstrate that the ESIPT process in Compound 2 occurs along this hydrogen bond to form a keto structure with an emission at 623 nm, which is consistent with the observed experimental value (634 nm). Therefore, the red-shift of the fluorescence of HBT-FS from 498 to 634 nm after adding F⁻ is caused by ESIPT. For SO3²⁻, orbital-weighted dual descriptor isosurface verifies that it is added to the C₅ site of HBT-FS and then forms Compound 3, which emits fluorescence at 404 nm. Thus, the experimentally measured fluorescence at 371 nm is assigned to Compound 3. In order to explain the blue-shift of the fluorescence of HBT-FS from 498 to 371 nm after adding SO₃²⁻, ICT is analyzed by frontier molecular orbitals and the isosurface of C₊ and C₋ functions. The analysis results demonstrate that ICT extent in Compound 3 is relatively weak compared with that in HBT-FS because of the destruction of the conjugated structure by the addition reaction of SO₃²⁻, which results in the



FIG. 8. The schematic diagram of fluorescence response mechanisms of HBT-FS for F⁻ and SO_3^{2-} . RGSIPT: Reverse ground state intramolecular proton transfer.

blue shift of fluorescence of HBT-FS. These different fluorescence responses make HBT-FS a fluorescent probe to discriminatorily detect F^- and SO_3^{2-} .

SUPPLEMENTARY MATERIAL

See the supplementary material for some functionals test results and IRC calculations.

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DATA AVAILABILITY

The data that supports the findings of this study are available within the article.

REFERENCES

- ¹M. Du, B. Huo, J. Liu, M. Li, L. Fang, and Y. Yang, "A near-infrared fluorescent probe for selective and quantitative detection of fluoride ions based on Si-Rhodamine," Anal. Chim. Acta. **1030**, 172–182 (2018).
- ²Z. J. Chen, Z. Tian, K. Kallio, A. L. Oleson, A. Ji, D. Borchardt, D. E. Jiang, S. J. Remington, and H. W. Ai, "The N–B interaction through a water bridge: Understanding the chemoselectivity of a fluorescent protein based probe for peroxynitrite," J. Am. Chem. Soc. 138, 4900–4907 (2016).
- ³Y. Nasu, Y. Asaoka, M. Namae, H. Nishina, H. Yoshimura, and T. Ozawa, "Genetically encoded fluorescent probe for imaging apoptosis in vivo with spontaneous GEP complementation," Anal. Chem. **88**, 838–844 (2016)
- spontaneous GFP complementation," Anal. Chem. 89, 838–844 (2016).
 ⁴X. Cheng, R. Tang, H. Jia, J. Feng, J. Qin, and Z. Li, "New fluorescent and colorimetric probe for cyanide: Direct reactivity, high selectivity, and bioimaging application," ACS. Appl. Mater. Inter. 4, 4387–4392 (2012).
- ⁵Y, Yu, H. Xu, W. Zhang, B. Wang, and Y. Jiang, "A novel benzothiazole-based fluorescent probe for cysteine detection and its application on test paper and in living cells," Talanta **176**, 151–155 (2018).
- ⁶L. Zhao, X. He, Y. Huang, J. Li, Y. Li, S. Tao, Y. Sun, X. Wang, P. Ma, and D. Song, "A novel ESIPT-ICT-based near-infrared fluorescent probe with large stokes-shift for the highly sensitive, specific, and non-invasive in vivo detection of cysteine," Sensor. Actuators, B **296**, 126571 (2019).
- ⁷Y. Li, J. F. Zhao, and T. S. Chu, "Glutathione sensing mechanism of a fluorescent probe: Excited state intramolecular proton transfer and photoinduced electron transfer," J. Lumin. **204**, 642–648 (2018).
- ⁸J. S. Chen, P. W. Zhou, S. Q. Yang, A. P. Fu, and T. S. Chu, "Sensing mechanism for a fluoride chemosensor: Invalidity of excited-state proton transfer mechanism," Phys. Chem. Chem. Phys. 15, 16183–16189 (2013).
- ⁹N. Zhao, Y. Li, Y. Jia, and P. Li, "Identifying the role of intramolecular charge transfer and excited-state proton transfer in fluorescence mechanism for an azido-based chemosensor," J. Phys. Chem. C 122, 26576–26583 (2018).
- ¹⁰X. L. Hao, Z. J. Guo, C. Zhang, and A. M. Ren, "Excellent benzocoumarinbased ratiometric two-photon fluorescent probe for H2O2 detection," Phys. Chem. Chem. Phys. 21, 281–291 (2019).
- ¹¹L. Li, Y. Zhang, Z. Chang, F. Q. Bai, H. X. Zhang, J. K. Ferri, and W. F. Dong, "Theoretical study on fluorescent probes for cyanide based on the indolium functional group," Org. Electron. **30**, 1–11 (2016).
- ²²M. H. Lu, P. W. Zhou, Z. W. Li, J. Y. Liu, Y. Q. Yang, and Kl Li, "New insights into the sensing mechanism of a phosphonate pyrene chemosensor for TNT," Phys. Chem. Chem. Phys. 20, 19539–19545 (2018).
- ¹³T. S. Chu, J. S. Chen, and Y. Li, "Sensing mechanism for a fluorescent off-on chemosensor for cyanide anion," J. Lumin. **179**, 203–210 (2016).
- ¹⁴B. Q. Sun, L. Liu, W. Liu, F. D. Meng, and Q. X. Huang, "ESIPT triggered TICT of an Al 3+ fluorescence sensor and its sensing mechanism," J. Lumin. 223, 117203 (2020).

- ¹⁵L. L. Lv, W. W. Luo, and Q. P. Diao, "A novel ratiometric fluorescent probe for selective detection and imaging of H₂S," Spectrochim. Acta, Part A. 246, 118959–118965 (2021).
- ¹⁶P. Kaur, R. Singh, V. Kaur, and D. Talwar, "Anthranilic acid Schiff base as a fluorescent probe for the detection of arsenite and selenite: A detailed investigation of analytical parameters and mechanism for interaction," Anal. Sci. 37, 553 (2021).
- ¹⁷G. J. Zhao, J. Y. Liu, L. C. Zhou, and K. L. Han, "Site-selective photoinduced electron transfer from alcoholic solvents to the chromophore facilitated by hydrogen bonding: A new fluorescence quenching mechanism," J. Phys. Chem. B 111, 8940–8945 (2007).
- ¹⁸J. Norell, M. Odelius, and M. Vacher, "Ultrafast dynamics of photo-excited 2thiopyridone: Theoretical insights into triplet state population and proton transfer pathways," Struct. Dyn. 7, 024101 (2020).
- ¹⁹M. Jen, K. Jeon, S. Lee, S. Hwang, W. Chung, and Y. Pang, "Ultrafast intramolecular proton transfer reactions and solvation dynamics of DMSO," Struct. Dyn. 6, 064901 (2019).
- ²⁰P. K. Verma, A. Steinbacher, A. Schmiedel, P. Nuernberger, and T. Brixner, "Excited-state intramolecular proton transfer of 2-acetylindan-1,3-dione studied by ultrafast absorption and fluorescence spectroscopy," Struct. Dyn. 3, 023606 (2016).
- ²¹J. F. Zhao, J. S. Chen, Y. L. Cui, J. Wang, L. X. Xia, Y. M. Dai, P. Song, and F. C. Ma, "A questionable excited-state double-proton transfer mechanism for 3-hydroxyisoquinoline," Phys. Chem. Chem. Phys. 17, 1142–1150 (2015).
- ²²J. F. Zhao, P. Song, Y. L. Cui, X. M. Liu, S. W. Sun, S. Y. Hou, and F. C. Ma, "Effects of hydrogen bond on 2-aminopyridine and its derivatives complexes in methanol solvent," Spectrochim. Acta, Part A. 131, 282–287 (2014).
- ²³Y. G. Yang, H. S. Zhai, Y. Liu, X. L. Jia, and Y. F. Liu, "Excited state intramolecular proton transfer induced fluorescent change and decay pathway of salicylideneaniline," J. Lumin. **216**, 116736 (2019).
- ²⁴Y. G. Yang, Y. Liu, H. S. Zhai, X. L. Jia, and K. Jiang, "Fluorescent behaviors and reaction mechanism of 10-hydroxybenzo [h]quinolone on the detection of phenylboronic acid," J. Lumin. 223, 117224 (2020).
- ²⁵Y. G. Yang, D. L. Li, C. Z. Li, Y. F. Liu, and K. Jiang, "Asymmetric substitution changes the UV-induced nonradiative decay pathway and the spectra behaviors of β-diketones," Spectrochim. Acta, Part A. 207, 209–215 (2019).
- ²⁶Y. Wang, Y. Shi, L. Cong, and H. Li, "TDDFT study of twisted intramolecular charge transfer and intermolecular double proton transfer in the excited state of 4'-dimethylaminoflavonol in ethanol solvent," Spectrochim. Acta, Part A 137, 913–918 (2015).
- ²⁷B. F. Cao, J. H. Han, Q. Zhou, C. F. Sun, Y. Li, B. Li, H. Yin, and Y. Shi, "Skillfully tuning 1-hydroxy-9H-fluoren-9-one forward-backward ESIPT processes by introducing electron-withdrawing groups: A theoretical exploration," J. Mol. Liq. **303**, 112627 (2020).
- ²⁸C. Z. Li, D. L. Li, C. Ma, and Y. F. Liu, "DFT-TDDFT investigation of excitedstate intramolecular proton transfer in 2–(2'-hydroxyphenyl) benzimidazole derivatives: Effects of electron acceptor and donor groups," J. Mol. Liq. 224, 83–88 (2016).
- ²⁹Q. Huang, X. F. Yang, and H. Li, "A ratiometric fluorescent probe for hydrogen sulfide based on an excited-state intramolecular proton transfer mechanism," Dyes Pigm. **99**, 871–877 (2013).
- ³⁰J. E. Kwon and S. Y. Park, "Advanced organic optoelectronic materials: Harnessing excited-state intramolecular proton transfer (ESIPT) process," Adv. Mater. 23, 3615–3642 (2011).
- ³¹J. Catalan, F. Fabero, R. M. Claramunt, M. D. Santa Maria, M. de la Concepcion Foces-Foces, F. H. Cano, M. Martinez-Ripoll, J. Elguero, and R. Sastre, "New ultraviolet stabilizers: 3- and 5-(2'-hydroxyphenyl)pyrazoles," J. Am. Chem. Soc. **114**, 5039–5048 (1992).
- ³²K. I. Sakai, T. Tsuzuki, Y. Ltoh, M. Ichikawa, and Y. Taniguchi, "Using protontransfer laser dyes for organic laser diodes," Appl. Phys. Lett. 86, 081103 (2005).
- ³³S. Sinha, B. Chowdhury, and P. Ghosh, "A highly sensitive ESIPT-based ratiometric fluorescence sensor for selective detection of Al³⁺," Inorg. Chem. 55, 9212–9220 (2016).
- ³⁴M. H. Lan, J. S. Wu, W. M. Liu, H. Y. Zhang, W. J. Zhang, X. Q. Zhuang, and P. F. Wang, "Highly sensitive fluorescent probe for thiols based on combination of PET and ESIPT mechanisms," Sens. Actuators, B 156, 332–337 (2011).

- ³⁵T. Mutai and K. Araki, "Synthesis of imidazopyridine derivatives showing efficient luminescence in the solid state-ESIPT luminescence properties and their crystal-structure dependence," J. Syn. Org. Chem. Jpn 75, 330–339 (2017).
- ³⁶M. J. Paterson, M. A. Robb, L. Blancafort, and A. D. Debellis, "Mechanism of an exceptional class of photostabilizers: A seam of conical intersection parallel to excited state intramolecular proton transfer (ESIPT) in o-Hydroxyphenyl-(1,3,5)-triazine," J. Phys. Chem. A 109, 7527–7537 (2005).
- ³⁷S. D. Liu, L. W. Zhang, P. P. Zhou, Y. Yang, and W. S. Wu, "Distinctive fluoride fluorescent probes with ratiometric characteristics combinate desilylation, hydrogen bond and ESIPT process: Spectral and mechanistic studies," Sens. Actuators, B 255, 401–407 (2018).
- ³⁸Y. C. Sun, Z. Chen, F. Z. Chen, H. Liu, H. P. He, X. H. Zhang, and S. F. Wang, "An HBT-based near-infrared fluorescent probe for colorimetric and ratiometric detection of bisulfite and its application in living cells," J. Fluoresc. 27, 1405–1411 (2017).
- ³⁹L. H. Geng, X. F. Yang, Y. G. Zhong, L. Zheng, and H. Li, "Quinone-phenol transduction activated excited-state intramolecular proton transfer: A new strategy toward ratiometric fluorescent probe for sulfite in living cells," Dyes Pigm. **120**, 213–219 (2015).
- ⁴⁰F. P. Qi, F. Zhang, L. N. Mo, X. J. Ren, Y. G. Wang, X. Li, X. J. Liu, Y. Zhang, Z. G. Yang, and X. Z. Song, "A HBT-based bifunctional fluorescent probe for the ratiometric detection of fluoride and sulphite in real samples," Spectrochim. Acta, Part A. 219, 547–551 (2019).
- ⁴¹C. Adamo and V. Barone, "Exchange functionals with improved long-range behavior and adiabatic connection methods without adjustable parameters: The mPW and mPW1PW models," J. Chem. Phys. **108**, 664–675 (1998).
- ⁴²A. Schäfer, C. Huber, and R. Ahlrichs, "Fully optimized contracted Gaussian basis sets of triple zeta valence quality for atoms Li to Kr," J. Chem. Phys. 100, 5829–5835 (1994).
- ⁴³V. Barone, R. Improta, and N. Rega, "Computation of protein pK's values by an integrated density functional theory/polarizable continuum model approach," Theor. Chem. Acc. 111, 237–245 (2004).

- ⁴⁴H. Li and J. H. Jensen, "Improving the efficiency and convergence of geometry optimization with the polarizable continuum model: New energy gradients and molecular surface tessellation," J. Comput. Chem. 25, 1449–1462 (2004).
- ⁴⁵M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian 16 Rev. B.01 Release Notes, Gaussian, Inc., Wallingford CT, 2016.
- ⁴⁶M. Barbatti, M. Ruckenbauer, F. Plasser, J. Pittner, G. Granucci, M. Persico, and H. Lischka, "Newton-X: A surface-hopping program for nonadiabatic molecular dynamics," Wiley Interdiscip. Rev.: Comput. Mol. Sci. 4, 26–33 (2014).
- ⁴⁷T. Lu and F. Chen, "Multiwfn: A multifunctional wavefunction analyzer," J. Comput. Chem. **33**, 580–592 (2012).
- ⁴⁸T. Lu and F. Chen, "Bond order analysis based on the Laplacian of electron density in fuzzy overlap space," J. Phys. Chem. A **117**, 3100–3108 (2013).
- ⁴⁹R. Pino-Rios, D. Inostroza, G. I. Cardenas-Jiron, and W. Tiznado, "Orbital-weighted dual descriptor for the study of local reactivity of systems with (quasi-) degenerate states," J. Phys. Chem. A 123, 10556–10562 (2019).
- 50T. L. Bahers, C. Adamo, and I. Ciofini, "A qualitative index of spatial extent in charge-transfer excitations," J. Chem. Theory Comput. 7, 2498–2506 (2011).