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All-optical switchings of 3-hydroxyflavone in different solvents*

Wu Feng(吴 峰)[a)b)], Lin Lie(林 列)[a)], Li Xiang-Ping(李向平)[a)],
Yu Ya-Xin(于雅鑫)[a)], Zhang Gui-Lan(张桂兰)[a)†], and Chen Wen-Ju(陈文驹)[a)]

[a)] *Institute of Modern Optics, Nankai University, Optoelectronics Information Science and Technology Laboratory, Ministry of Education, Tianjin* 300071, *China*

[b)] *Department of Physics, North University of China, Taiyuan* 030051, *China*

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3-hydroxyflavone (3-HF) is an organic molecule with an excited-stated intramolecular proton transfer (ESIPT) effect. All-optical switchings and beam deflections of 3-HF in three kinds of solvents (cyclohexane, ethanol and dimethyl sulfoxide) have been investigated by using the third-harmonic generation (355 nm) of a mode-locked Nd:YAG laser as a pump beam and a continuous-wave (cw) He-Ne laser (632.8 nm) as a probe beam. The nonlinear refractive indices of 3-HF in the three different solvents are determined by using the Z-scan technique under an ultraviolet (UV) pump beam at a wavelength of 355 nm. It has been found that the optical switching and beam deflection effects result from the change in refractive index of 3-HF under the irradiation of the pump beam. On the basis of the analyses of absorption spectra and fluorescence spectra, we conclude that the change in refractive index of 3-HF is due to not the thermal effect but the ESIPT effect of 3-HF under the pump beam. As the ESIPT is exceedingly fast, 3-HF might be an excellent candidate for high-speed optical switching.

Keywords: all-optical switching, 3-hydroxyflavone, ESIPT, nonlinear
PACC: 7865P, 7800, 4265

1. Introduction

All-optical switchings are fundamental building blocks for future high-speed optical networks. They are playing an important role in the optical information processing, optical computation and optical communication.[1−3] Therefore, the investigation of all-optical switching characteristics is of considerable importance and has attracted much attention of many scientists. The optical switching property is closely related to the material of a device. Many materials for optical switching devices have been reported, including inorganic and semiconductor materials,[4−6] multiple quantum wells,[7,8] photonic crystal,[9−11] organic polymers[12−15] and so on. However, few studies are concerned with organic-molecular-based devices possessing excited-stated intramolecular proton-transfer (ESIPT) effect. Recently, our research group has reported all-optical switching effects of some organic molecules with ESIPT effect and obtained some significant results.[16,17]

3-hydroxyflavone (3-HF) is a typical compound undergoing an ESIPT process. A simplified model of the proton transfer cycle is depicted in Fig.1. When an exciting light irradiates the molecule, it is excited to an excited state and the hydroxyl proton of the molecule transfers to an acceptor, another adjacent oxygen atom of the molecule through the intramolecular H-bond. The molecule transforms from the excited state of the normal form (N*) into the excited state of its tautomeric form (T*). The excited state of the tautomer decays to the ground state accompanied with the emission of fluorescence or with a nonradiative transition, and then it returns to the ground state of the normal form(N). As the ESIPT effect results in the population change and the relaxation of several electronic states of the molecular, which causes a change in refractive index of the molecule, time-resolved studies have shown that this process of ESIPT is exceedingly fast, less than a picosecond or even on the time scale of subpicosecond.[18] Therefore, the 3-HF could be an excellent optical material for various types of photo-electronic devices.

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†Corresponding author. E-mail: zhanggl@nankai.edu.cn or ourdaywufeng2000@163.com

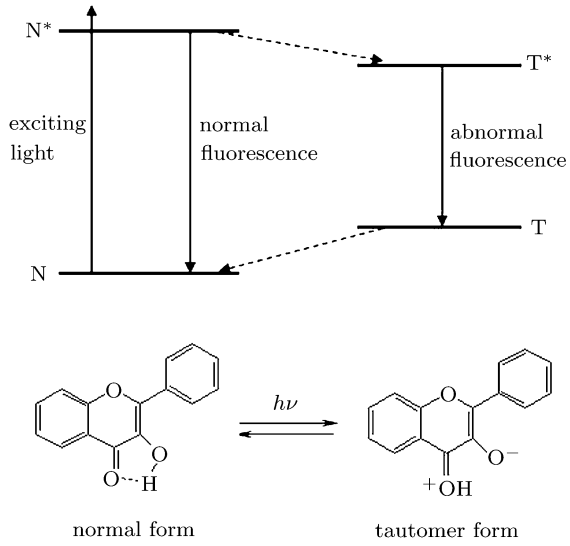


Fig.1. Molecular structure and relevant energy levels of the normal form and tautomer form.

In this paper, we have investigated the optical switchings and beam deflections of 3-HF in different solvents by using a cw He-Ne laser as a probe beam under a UV pump beam at 355 nm and determined the nonlinear refractive indices by the Z-scan technique. Through the analyses of the absorption spectra and the fluorescence spectra of 3-HF in different solvents, we verify that the nonlinear refractive index and the optical switching of 3-HF solution are dominantly due to the ESIPT effect of the molecule.

2. Experiments and results

2.1. Sample preparation

The 3-HF is the product of the Acros Company and is purified by recrystallization before use. Analytical reagent(AR) cylcohexane, ethanol and dimethyl sulfoxide (DMSO) served as solvent. The concentrations of 3-HF solutions all are 1×10^{-4}mol/L. All the solutions are kept in the dark before use.

2.2. All-optical switching phenomena of 3-HF in different solvents

The experimental setup for observing the optical switching of 3-HF solution is shown in Fig.2. The 355 nm pump beam is the third-harmonic generation of a mode-locked Nd:YAG laser (YG901C, Quantel Co.), which generates 35 ps laser pulses operating at 10Hz repetition rate. The output energy of the laser pulse is attenuated to 50 μJ per pulse. An electronically controlled shutter is used to ensure that only

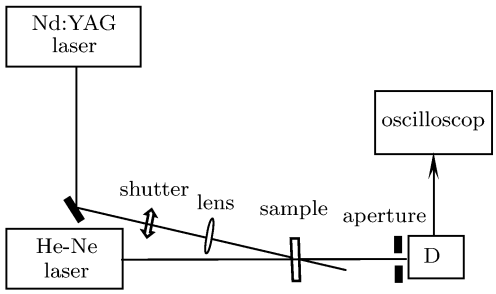


Fig.2. Experimental setup of optical switching of 3-HF solution.

one laser pulse arrives at a 1 mm thick quartz cell with 3-HF solution every three seconds. In order to obtain good results of the on-off contrast ratios, the appropriate distance between sample and aperture is 0.3 m. The probe beam, which is provided by a 20 mW cw He-Ne laser (632.8 nm), intersects the probe beam in the sample cell filled with 3-HF solution. When the pump beam is shut off by the shutter, the probe beam passes through the sample cell and aperture A, and then it is received by a photomultiplier (PMT), which provides an electrical signal to a digital oscilloscope (TSD3052B, Tektronix). Thus, with the shutter closed, the oscilloscope shows a horizontal straight line (a high electrical level). When the shutter isopened, the pump beam works and the probe beam is deflected from its course inside the sample cell and propagates away from aperture A. The signal on the screen of the oscilloscope suddenly falls from a high electrical level to a low electrical level (switch 'off' state) and a "sharp decline" phenomenon appears on the screen of the oscilloscope immediately. Subsequently, it returns to a high level gradually, and a "tail phenomenon" appears on the screen of the oscilloscope after the pump beam dies away. The optical switching phenomena of 3-HF in the three kinds of solvents are shown in Fig.3. The start-up (from the 'on' state to 'off' state) lies on the response time of the ESIPT of 3-HF as reported in Ref.[19]. So the start-up shows a sharp decline in that the ESIPT rate is very fast (on the picosecond time scale). The characteristic recovery time depends on the heat diffusion of the solution. It can be estimated by the relation $t = \omega_0^2\rho C_p/4\kappa$,[20,21] where ω_0 is the radius of the probe beam, ρ is the liquid density, $C_{\rm p}$ is the specific heat at constant pressures and κ is the thermal conductivity. In our experimental setup, by reason of the large radius of the probe beam in DMSO ($\omega_0 = 1$mm), the recovery time (from the 'off' state to 'on' state) is very long ($t = 2.36$ s).This calculated result is in close agreement with the experimental result

as we obtained in Fig.3. By reducing the beam radius to 0.5 mm in DMSO, we can achieve a short recovery time $t = 0.60$ s as shown in Fig.4. Moreover, we obtain the similar results in ethanol and cylcohexane under the same condition, indicating the characteristic recovery time is dominated by the heat diffusion of the solution. For a quantitative comparison of optical switching of 3-HF, the on-off contrast ratios of the optical switchings in the different solvents are calculated by the relation $C = \dfrac{\Delta L_2}{\Delta L_1} = \dfrac{L_1 - L_2}{L_1 - L_0}$, where L_0 is the electronic level of the intrinsic noise signal, L_1 is the high level, with pump beam closed, and L_2 is the low level while the pump beam and probe beam are open.

Table 1. On-off contrast ratios of optical switchings of 3-HF in different solvents.

Solvent	cyclohexane	ethanol	DMSO
On-off contrast ratio/dB	6.02	3.97	2.68

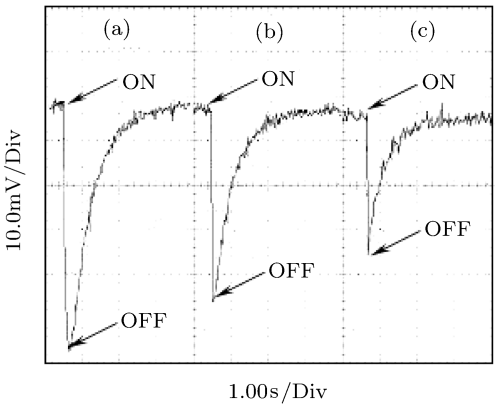


Fig.3. Optical switching effects of 3-HF in different solvents ($\omega_0 = 1$mm). (a) Cyclohexane; (b) ethanol; (c) DMSO.

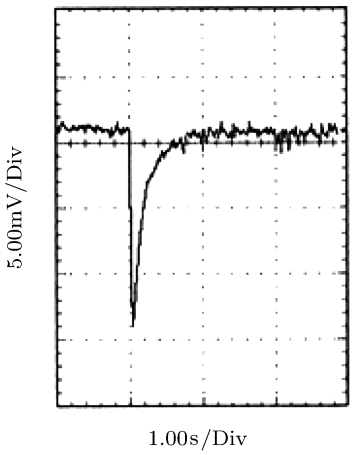


Fig.4. Optical switching effect of 3-HF in DMSO ($\omega_0 = 0.5$mm).

The illustration of on-off contrast ratio is given in Fig.5. The calculated results are listed in Table 1. As shown in Table 1, the contrast ratio of 3-HF in cyclohexane is the largest, and that in DMSO is the smallest.

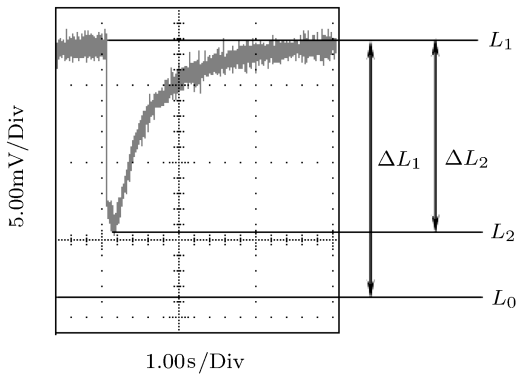


Fig.5. Illustration of on-off contrast ratio.

2.3. Optical beam deflections of 3-HF in different solvents

In the experimental setup (Fig.2), we take away the aperture and locate a screen at a distance of 4.0 m away from the sample cell to observe the beam deflection. The modified experimental setup is schematically illustrated in Fig.6. When the shutter is closed, the probe beam passes through the sample cell and reaches point A. When the shutter is opened, the probe beam is deflected inside the sample cell and reaches point B. The distances between points A and B are different for 3-HF in different solvents. According to the distance AB, the deflection angle θ can be obtained. The measurement results are shown in Table 2. The deflection angle θ for 3-HF in cyclohexane is the largest and that for 3-HF in DMSO is the smallest. These results are consistent with the results of optical switching effects described above.

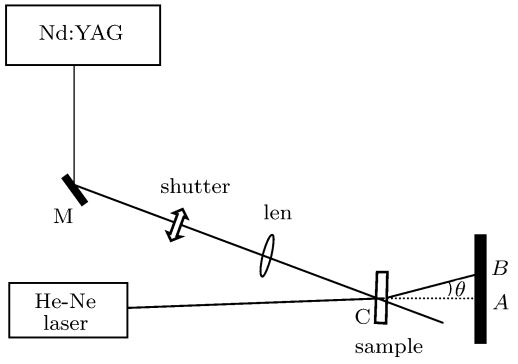


Fig.6. Experimental setup of probe beam deflection of 3-HF solution.

Table 2. The values of deflection angle θ of 3-HF in different solvents.

Solvent	cyclohexane	ethanol	DMSO
Deflection angle θ/rad	0.71	0.59	0.41

2.4. Nonlinear refractive indices of 3-HF in different solvents

The nonlinear refractive index n_2 of 3-HF are determined by using the Z-scan technique. The Z-scan experimental setup as shown in Fig.7, is based on a mode-mocked Nd:YAG laser (YAG901C, Quantel Co.). The incident light source is the third harmonic generation (SHG) of the Nd:YAG laser operating at a 355 nm wavelength, 35 ps pulse width, and 10 Hz repetition. The output energy of the laser pulse is attenuated to 50 μJ per pulse. The output beam of the laser is split into two beams by a beam splitter BS. One is detected by a detector D_1 (J25LP-3, Molectron Co.) as a reference beam, and the other is focused on a 1mm thick quartz sample cell S containing 3-HF solution with lens L (f = 250mm). The sample cell is moved by a stepping motor along the Z direction through the focal point. The Z-scan signal is received by a detector D_2 (J309, Molectron Co.) with an aperture of a linear transmittance of 0.1. A laser energy meter (EMP2000, Molectron Co.) is used to measure the Z-scan signal from D_2 and monitor the reference light signal from D_1 simultaneously. For the sake of avoiding the thermal cumulative effect, an electronically controlled shutter M is used to ensure that only one laser pulse arrives at the sample cell every three seconds. Furthermore, before the Z-scan experiment we have carefully calibrated the measurement system by using the standard reference material CS_2 for ensuring the accuracy of the experiment. The theoretical fitting value of the Z-scan data is $n_2 = 9.3 \times 10^{-12}$esu at 532 nm, which is in close agreement with the value given in Ref.[22] ($n_2 = 1.2 \times 10^{-11}$esu). In order to reduce the error, each experimental data point is averaged over 20 pulses, and the relative error is about 3.6%. So the measured data have a high reliability and repeatability. The Z-scan curve of 3-HF in cyclohexane is shown in Fig.8. The curve shows a peak-valley configuration, which indicates the negative sign of the nonlinear refractive index. The Z-scan curves of 3-HF in DMSO and in ethanol are similar to those in Fig.8.

The nonlinear refractive index n_2 is defined as

$$n = n_0 + n_2 I, \tag{1}$$

where n is the total refractive index, n_0 is linear refractive index, and I is the intensity of the incident light within the sample. Based on the Z-scan theory, in the case of the small phase change ($|\Delta\Phi_0| \ll 1$), the normalized transmittance can be given by[22]

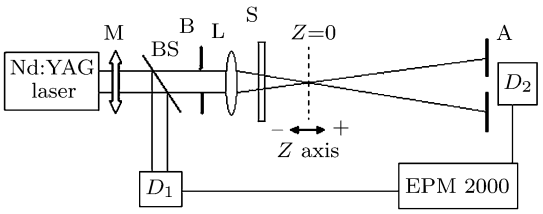


Fig.7. Experimental setup of Z-scan technique.

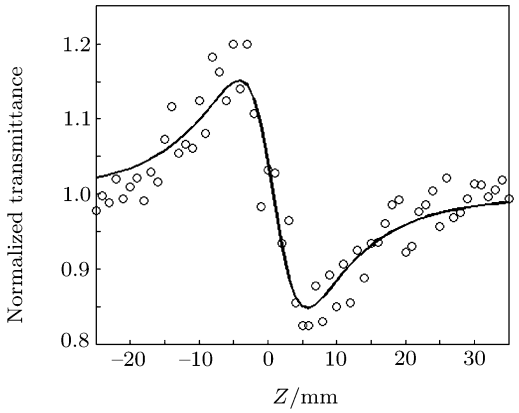


Fig.8. Z-scan curve of 3-HF in cyclohexane. The scattered points are experimental data and the solid line is theoretically fitting curve.

$$T(z) = 1 + \frac{4\langle\Delta\Phi_0(t)\rangle(z/z_0)}{(z^2/z_0^2+9)(z^2/z_0^2+1)} \tag{2}$$

with

$$\Delta\Phi_0(t) = kn_2 I_0(t) L_{\text{eff}}, \tag{3}$$

where $z_0 = \frac{1}{2}k\omega_0^2$ is the diffraction length, z is the distance from the sample to focus, $\langle\Delta\Phi_0(t)\rangle$ is the on-axis time-averaged phase shift at the focus, k is the wave vector, $I_0(t)$ is the on-axis intensity at focus (i.e. $z = 0$), $L_{\text{eff}} = [1 - \exp(-\alpha L)]/\alpha$ denotes the effective length of the sample with α being linear absorption coefficient and L the sample length. The value of $\langle\Delta\Phi_0(t)\rangle$ can be obtained from Eq.(2) by fitting the experimental Z-scan data, and using Eq.(3) we can obtain the values of n_2 of 3-HF in different solvents. Using a pure solvent as the sample, the value of n_2

of pure solvent can be determined. The experimental results show that the value of n_2 of pure solvent is much smaller than that of 3-HF solution, so that the contribution of solvent to n_2 of 3-HF solution can be ignored. At last, the values of the nonlinear refractive index n_2 of 3-HF in different solvents are summarized in Table 3.

Table 3. The values of nonlinear refractive index n_2 of 3-HF in different solvents.

Solvent	cyclohexane	ethanol	DMSO
$n_2/\times 10^{-21}$(SI)	−(3.66±0.13)	−(4.14±0.15)	−(4.60±0.17)

2.5. Absorption spectra and fluorescence spectra of 3-HF in different solvents

The absorption spectra of 3-HF solution are recorded with a UV-Vis spectrophotometer (WF2-25A, made in China). Figure 9 presents the absorption spectra of 3-HF in the three different solvents. The absorption spectral configurations of 3-HF in the three kinds of solvents are similar to each other. All of them have a strong absorption band from 300 nm to 375 nm, which is assigned to the $\pi \rightarrow \pi^*$ transition of the normal form of 3-HF. But the absorbances of 3-HF are quite different in three different solvents. The extinction coefficients at 355 nm (ε_{355}) of 3-HF solutions were measured as listed in Table 4. As shown in Table 4, the extinction coefficient ε_{355} in cyclohexane is the smallest and that in ethanol is the largest.

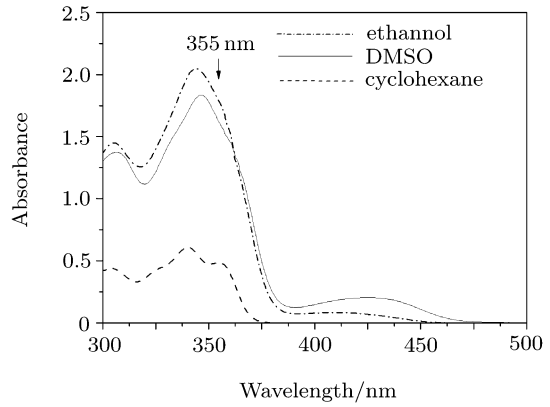


Fig.9. Absorption spectra of 3-HF in different solvents.

Table 4. Extinction coefficient ε_{355} of 3-HF in different solvents.

Solvent	cyclohexane	ethanol	DMSO
$\varepsilon_{355}/\mathrm{M}^{-1}\mathrm{cm}^{-1}$	0.48	1.77	1.60

The fluorescence spectra of 3-HF are recorded on an RF540 fluorescence spectrophotometer (Shimadzu Co.). As shown in Fig.10, there appear two fluorescence bands. One is at about 410 nm and attributed to the emission from the excited normal form (N^*) (see Fig.1), and it is referred to as normal fluorescence band, and the other is at about 520 nm and attributed to the emission from the excited tautomer form (T^*) generated via ESIPT, and it is referred to as abnormal fluorescence (ESIPT fluorescence) (see Fig.1).Therefore, the ratio of the intensity at 520 nm to the intensity at 410 nm may be used to estimate the efficiency of ESIPT. The ESIPT efficiency η can be determined by the following equation:

$$\eta = I_a/(I_n + I_a), \tag{4}$$

where I_n is the normal fluorescent intensity at 410 nm, and I_a is the ESIPT fluorescence intensity at 520 nm. The calculated results of η are indicated in Table 5. As shown in Table 5, the ESIPT efficiency of 3-HF in cyclohexane is the largest and almost 100%, which means that few 3-HF molecules exist in the normal form and all the 3-HF molecules are almost transformed from the normal form into their tautomeric form via ESIPT under the pump beam. The ESIPT efficiency of 3-HF in DMSO is smaller than that in ethanol, which means that the number of 3-HF molecules in the normal form in DMSO are more than in ethanol. So the ESIPT efficiency can reveal some changes of 3-HF molecular between in the normal form and in their tautomer form during the ESIPT process.

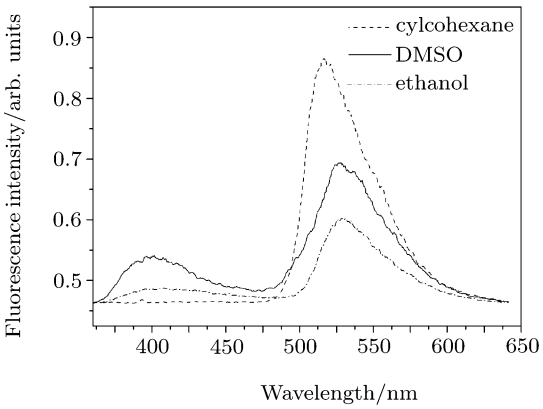


Fig.10. Fluorescence spectra of 3-HF in different solvents (λ_{ex}=355 nm).

Table 5. ESIPT efficiency η of 3-HF in different solvents.

Solvent	cyclohexane	ethanol	DMSO
η/%	100	67	62

3. Discussion and conclusion

The optical switching effect of 3-HF originates from the deflection of the probe beam, and the latter results from the change in refractive index of 3-HF under the irradiation of the pump beam. In our work, 3-HF is dissolved in three species of solvent, i.e. nonpolar solvent cyclohexane, polar solvent ethanol and strong polar solvent DMSO. Of the three solvents the nonlinear refractive index of 3-HF in cyclohexane is the largest, so the deflection angle of the probe beam and the on-off contrast ratio of the optical switching are the largest for 3-HF in cyclohexane. The nonlinear refractive index of 3-HF in DMSO is the smallest, so the deflection angle of the probe beam and the on-off contrast ratio of the optical switching effect are the smallest. The situation of 3-HF in ethanol is between the above two cases.

In the present work, there might be two reasons why the 3-HF solution takes on a large nonlinear refractive index: one is the thermal effect that is due to the absorption of the pump beam, and the other is the ESIPT effect of 3-HF. As for the thermal effect, of the three solvents, the extinction coefficient ε_{355} in ethanol is the largest but that in cyclohexane is the smallest. This result implies that 3-HF in ethanol should exhibit the largest thermal-effect induced nonlinear refractive index and the smallest one in cyclohexane. But it is not consistent with the magnitude order of the nonlinear refractive index of 3-HF in each solvent. Hence the thermal effect is not caused mainly by the nonlinear refractive index of 3-HF. As for the ESIPT effect, 3-HF molecule in the polar solvent ethanol and the strong polar solvent DMSO tends to become the normal solvated form via intermolecular H-bond. The normal solvated form can prevent the ESIPT from occurring. As a result, the ESIPT efficiency decreases with the enhancement of the solvent polarity.[23] The stronger the solvent polarity, the lower the ESIPT efficiency. The ESIPT efficiency of 3-HF in cyclohexane is the largest and that in DMSO is the smallest. It accords with the result of the nonlinear refractive index of 3-HF. Namely, the higher the ESIPT efficiency, the larger the nonlinear refractive index. It follows that the nonlinear refractive index of 3-HF originates from the ESIPT effect under the pump beam.

In conclusion, the duration of the ESIPT process is less than a picosecond and the efficiency of ESIPT is very high, so the 3-HF could be an excellent candidate material for optical switching devices with high speed and high sensitivity.

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