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Optical switching of 2-(2′-hydroxyphenyl) benzoxazole in different solvents

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ABSTRACT All-optical switching and beam deflection of 2-(2′-hydroxyphenyl) benzoxazole (HBO) in three species of solvent (cyclohexane, ethanol and dimethyl sulfoxide) have been investigated by using third-harmonic generation (355 nm) of a mode-locked Nd:YAG laser as a pump beam and a continuous-wave He-Ne laser (632.8 nm) as a probe beam. The nonlinear refractive indices of HBO in different solvents are determined by using the Z-scan technique. The optical switching and beam-deflection effects are due to the change of the refractive index of HBO under the pump beam. Through the study of the absorption spectra and the fluorescence spectra of HBO in different solvents, we conclude that the principal reason for the change of the refractive index of HBO is not the thermal effect because of absorption of the pump beam, but the excited-state intramolecular proton-transfer (ESIPT) effect of HBO under the pump beam. As the ESIPT process is very fast, HBO might be an excellent material for high-speed optical switching.

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1 Introduction

High-speed and high-sensitivity optical devices play an important role in optical information processing, optical computation and optical communication. Therefore, the study of all-optical switching characteristics is of importance. The optical switching property is closely concerned with the material of the device. Many materials for optical switching devices have been reported, including inorganic and semiconductor materials [1–3], multiple quantum wells [4, 5], liquid crystals [6, 7], organic compounds [8, 9], polymers [10, 11] and so on. However, devices based on organic molecules with excited-state intramolecular proton transfer (ESIPT) have been little reported. Recently, we have reported the optical switching effect of 7-hydroxyquinoline, a kind of molecule with ESIPT [12].

When exciting light irradiates a molecule with ESIPT, such as 2-(2′-hydroxyphenyl) benzoxazole (HBO), the molecule is driven to the excited state and a hydroxyl proton of the molecule is transferred to an acceptor, such as a nitrogen atom. The molecule transforms from the excited state of the normal molecule (enol form) into the excited state of its tautomer (keto form). The duration of this process is about or less than a picosecond. The excited state of the tautomer decays to its ground state with the emission of fluorescence or by a nonradiative transition and then returns to the ground state of the normal form [13–15] (cf. Fig. 6). As the ESIPT results in the population and relaxation of several electronic states, which cause a change in the refractive index of the molecule, the molecule with ESIPT should be an excellent nonlinear optical material for high-speed and high-sensitivity optical switching devices.

In this paper, we have investigated the optical switching and beam deflection of HBO in different solvents under a UV pump beam and determined their nonlinear refractive indices by the Z-scan technique. Through the study of the absorption spectra and the fluorescence spectra of HBO in different solvents, we verify that the origin of the nonlinear refractive index and the optical switching of HBO solutions is dominantly due to the ESIPT effect of the molecule.

2 Experiments and results

2.1 *Sample preparation*

Commercially available HBO (Aldrich Chemical Co., Milwaukee, WI) was purified by recrystallization before use. Spectrograde cyclohexane, ethanol and dimethyl sulfoxide served as solvents. The concentrations of HBO solutions all were 2×10^{-2} M. All the solutions were kept in the dark before use.

2.2 *All-optical switching phenomena of HBO in different solvents*

The experimental setup for observing the optical switching of an HBO solution is shown in Fig. 1. A mode-locked Nd:YAG laser (YG901C, Quantel Co.) with second-harmonic generation (SHG) (532 nm) and third-harmonic generation (THG) (355 nm), which generates 35 ps laser pulses operating at 10 Hz repetition rate, is provided as a pump beam. The output energy of the laser pulse is attenuated to 100 μJ per pulse. An electronically controlled shutter is used to ensure that only one laser pulse arrives at the sample cell every three seconds. A continuous-wave

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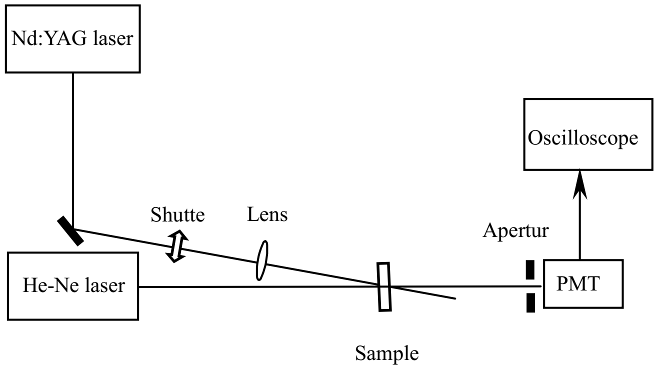

FIGURE 1 Experimental setup of optical switching of HBO solution

(cw) He-Ne laser (632.8 nm) is used as a probe beam. The pump beam intersects the probe beam in a 1.5 mm thick sample cell, which contains the HBO solution. When the pump beam is off, the probe beam passes through the sample cell and the aperture A, and is then received by a photomultiplier (R456), which provides an electrical signal to an oscilloscope (TDS520c, Tektronix). Thus, with the shutter closed, a signal level (horizontal straight line) appears on the screen of the oscilloscope. When the THG laser (355 nm) is used as the pump beam and the shutter is opened, the probe beam is deflected from its course inside the sample cell and propagates away from the aperture A. The signal on the screen of the oscilloscope falls off suddenly and it then returns to the original level gradually as the laser pulse of the pump beam dies away. The optical switching phenomena of HBO in three species of solvent are shown in Fig. 2. The signal does not return immediately to the original level and a "tail phenomenon" appears after the pump beam pulse dies away. It is due to the fact that the characteristic switch-off time is determined by heat diffusion of the solution [16]. It can be estimated by using the relation $t = \omega_0^2 \varrho C_\mathrm{p}/4\kappa$, where ω_0 is the beam-spot size, ϱ is the liquid density, C_p is the specific heat at constant pressure and κ is the thermal conductivity. Because the beam-spot size ω_0 in our experimental setup is very large ($\omega_0 = 2\,\mathrm{mm}$), the 'tail' is very long ($t > 500\,\mathrm{ms}$). By reducing the beam-spot size, we can get a short 'tail' [16]. The on–off contrast ratios of the optical switching of HBO in different solvents are given in Table 1. The contrast ratio for HBO in cyclohexane is larger than that in ethanol and that in dimethyl sulfoxide. Moreover, using a cw Ar^+ laser (514.5 nm or 488.0 nm) as a probe beam, we can also obtain similar results described above. Any wavelength of visible light can be used as a probe beam. Due to the limitation of space, in this paper we do not intend to report the results about the Ar^+ laser; only the He-Ne laser is mentioned. Under the same experimental condition, using the SHG laser (532 nm) as the pump beam, we did not find the optical switching phenomenon for all HBO solutions.

Solvent	Cyclohexane	Ethanol	Dimethyl sulfoxide
Contrast ratio (dB)	19	9	6

TABLE 1 On–off contrast ratio of optical switching of HBO in different solvents

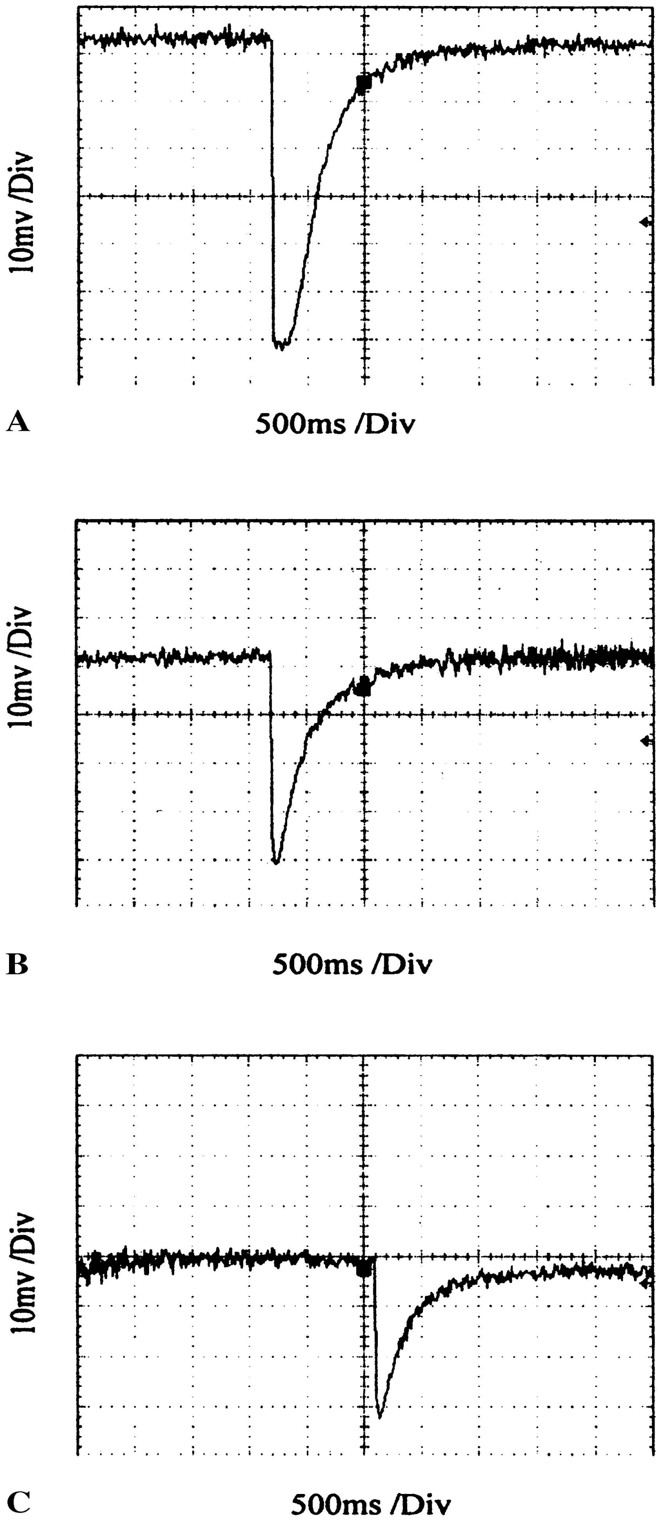

FIGURE 2 Optical switching effect of HBO in different solvents. **A** cyclohexane, **B** ethanol, **C** dimethyl sulfoxide

2.3 *Optical beam deflection of HBO in different solvents*

In the experimental setup (Fig. 1), we put a screen in the position of the aperture A to observe the probe-beam deflection. When the pump beam is off, the probe beam passes through the sample cell and reaches the point A (linear propa-

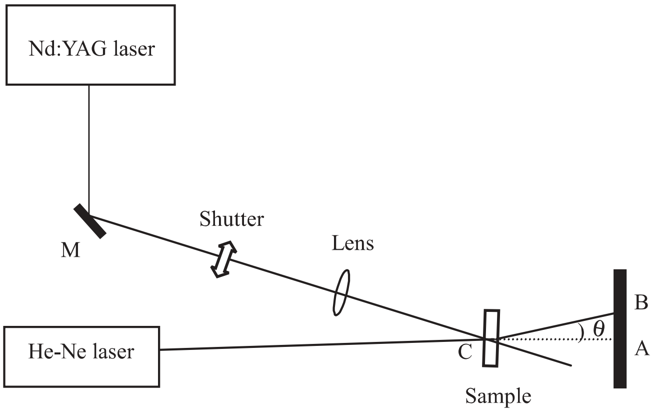

FIGURE 3 Illustration of optical beam deflection of HBO solution, CA linear propagation, see text; CB nonlinear propagation, see text

Solvent	Cyclohexane	Ethanol	Dimethyl sulfoxide
Deflection angle (θ^0)	0.024	0.014	0.010

TABLE 2 Size of optical beam deflection of HBO in different solvents

gation). When the THG laser is used as the pump beam and the shutter is opened, the probe beam is deflected inside the sample cell and reaches point B (nonlinear propagation). The experiment is schematically illustrated in Fig. 3. The size of the deflection angle θ of the probe beam is different for different HBO solutions. The measurement results are given in Table 2. The deflection angle θ for HBO in cyclohexane is the largest and that for HBO in dimethyl sulfoxide is the smallest. Using a SHG laser as the pump beam, we did not find the optical beam deflection of the probe beam for all HBO solutions. These results are in agreement with the results of the optical switching described above.

2.4 *Nonlinear refractive indices of HBO in different solutions*

The nonlinear refractive indices n_2 of HBO in different solvents were determined by using the Z-scan technique. The experimental setup is shown in Fig. 4. The incident light source is THG of a Nd:YAG laser (YG901C, Quantel Co.) operating at 355 nm wavelength, 35 ps pulse width, 10 Hz repetition rate and 100 μJ per pulse. The output beam of the laser is split into two beams by a beam splitter BS. One beam is detected by a detector (J25LP-3, Molectron Co.) as the reference beam. The other beam is focused on a 1 mm thick sample cell with a lens L ($f = 300$ mm). The sample cell is moved by a stepping motor along the Z direction. The Z-scan signal is received by a detector (J3-09, 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 and to monitor the reference light intensity simultaneously. Figure 5 shows the experimental Z-scan curve of HBO in cyclohexane. The curve shows a valley–peak configuration. It means that the nonlinear refractive index n_2 of HBO is positive. The Z-scan curves of HBO in ethanol and in dimethyl sulfoxide are similar to Fig. 5.

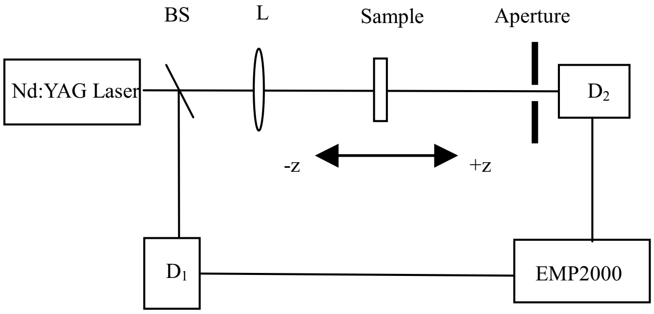

FIGURE 4 Experimental setup of Z-scan technique

Under the thin-sample approximation and the far-field case, the following conditions should be satisfied [17]: $L < Z_0/\Delta\Phi_0$ and $d \gg Z_0$, where $Z_0 = \kappa\omega_0^2/2$ is the diffraction length and ω_0 and κ are the waist radius of the Gaussian beam and the wave vector, respectively. L is the length of the sample, d is the distance between the sample and the detector and $\Delta\Phi_0$ is the on-axis phase shift at the focus. Then, the normalized transmittance of the Z-scan curve is given by

$$T\left(Z, \Delta\Phi_0\right) = 1 + \frac{4\Delta\Phi_0 x}{\left(x^2+9\right)\left(x^2+1\right)}, \tag{1}$$

with

$$\Delta\Phi_0 = \kappa n_2 I_0 L_{\mathrm{eff}}\,, \tag{2}$$

where $x = Z/Z_0$, I_0 is the on-axis intensity in the focus plane, n_2 is the nonlinear refractive index and $L_{\mathrm{eff}} = \left[1-\exp\left(-\alpha L\right)\right]/\alpha$, with α the linear absorption coefficient. The relationship between the nonlinear refractive index n_2 and the total refractive index n of the sample is as follows:

$$n\left(I\right) = n_0 + \Delta n = n_0 + n_2 I, \tag{3}$$

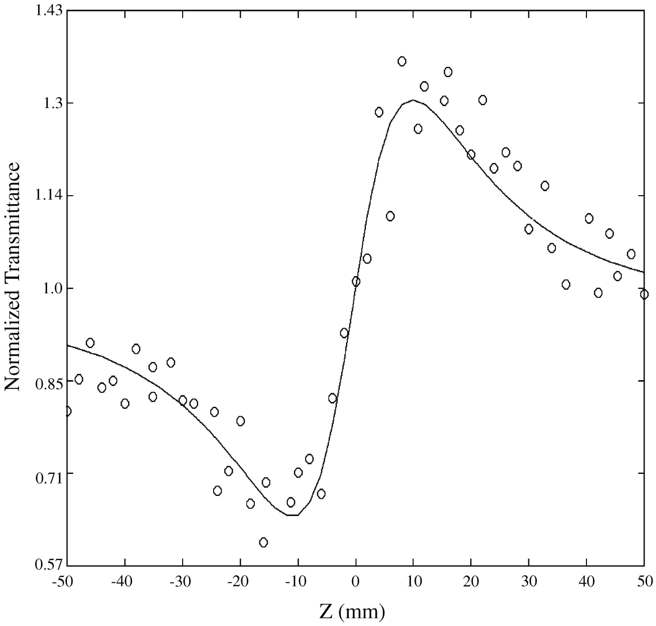

FIGURE 5 Z-scan curve of HBO in cyclohexane. *Circles* represent experimental data and *solid curve* is the theoretical fitting curve

Solvent	Cyclohexane	Ethanol	Dimethyl sulfoxide
$n_2 \times 10^{-13}$ esu	6.71	6.15	5.99

TABLE 3 Nonlinear refractive index n_2 of HBO in different solvents

where n_0 is the linear refractive index and I is the intensity of the laser beam within the sample. The value of $\Delta\Phi_0$ can be obtained from (1) by fitting the experimental Z-scan curve, and using (2) we can obtain the nonlinear refractive indices n_2 of HBO in different solvents, which are given in Table 3. Using pure solvent as the sample, the value of n_2 of the pure solvent can be determined. The experimental results show that the value of n_2 of the pure solvent is much less than that of HBO solution, so that the contribution of the pure solvent to n_2 of the HBO solution could be ignored.

2.5 *Absorption spectra and fluorescence spectra of HBO in different solvents*

The HBO solutions have a strong and broad absorption band in 250–420 nm [13, 14]. These results show that any visible light with a wavelength larger than 420 nm is transparent for the HBO solutions and can be used as a probe beam, but cannot be used as a pump beam. The shapes of the absorption bands for HBO in different solvents are almost the same but the absorption coefficients are slightly different. The extinction coefficients at 355 nm (ε_{355}) of HBO in different solvents were measured on a UV-Vis spectrophotometer (WF2-25A, made in China). The results are listed in Table 4. The extinction coefficient ε_{355} of HBO in dimethyl sulfoxide is the largest and that of HBO in ethanol is the smallest.

The fluorescence spectra of HBO solutions were observed on an RF540 fluorescence spectrophotometer (Shimadzu Co.) as shown in Fig. 6. Two fluorescence peaks usually appear at ~ 430 nm and 500 nm. The fluorescence band at 430 nm is the emission band of the excited enol form of HBO, and it is referred to as the normal fluorescence band. The fluorescence band at 500 nm is the emission band of the excited keto form of HBO, and it is usually referred to as the abnormal or ESIPT fluorescence band [13, 14] (cf. Fig. 6B). In the fluorescence spectrum of HBO in dimethyl sulfoxide, the normal band is very strong and the abnormal band is very weak, which means that a great deal of the HBO molecules are still in enol form and only a few of the HBO molecules transform to the keto form via ESIPT under the pump beam. In the fluorescence spectrum of HBO in cyclohexane, the abnormal band is very strong and the normal band nearly disappears, which means that the great majority of the HBO molecules transform to the keto form via ESIPT under the pump beam. Therefore, the ratio of the intensity at 500 nm to the intensity at 430 nm may be used to estimate the efficiency of ESIPT. From Fig. 6, we can see that the efficiency of ESIPT of HBO in cyclohexane is the largest and that of HBO in dimethyl sulfoxide is the smallest.

Solvent	Cyclohexane	Ethanol	Dimethyl sulfoxide
ε_{355}	3.000	1.550	9.125

TABLE 4 Extinction coefficients ε_{355} of HBO in different solvents

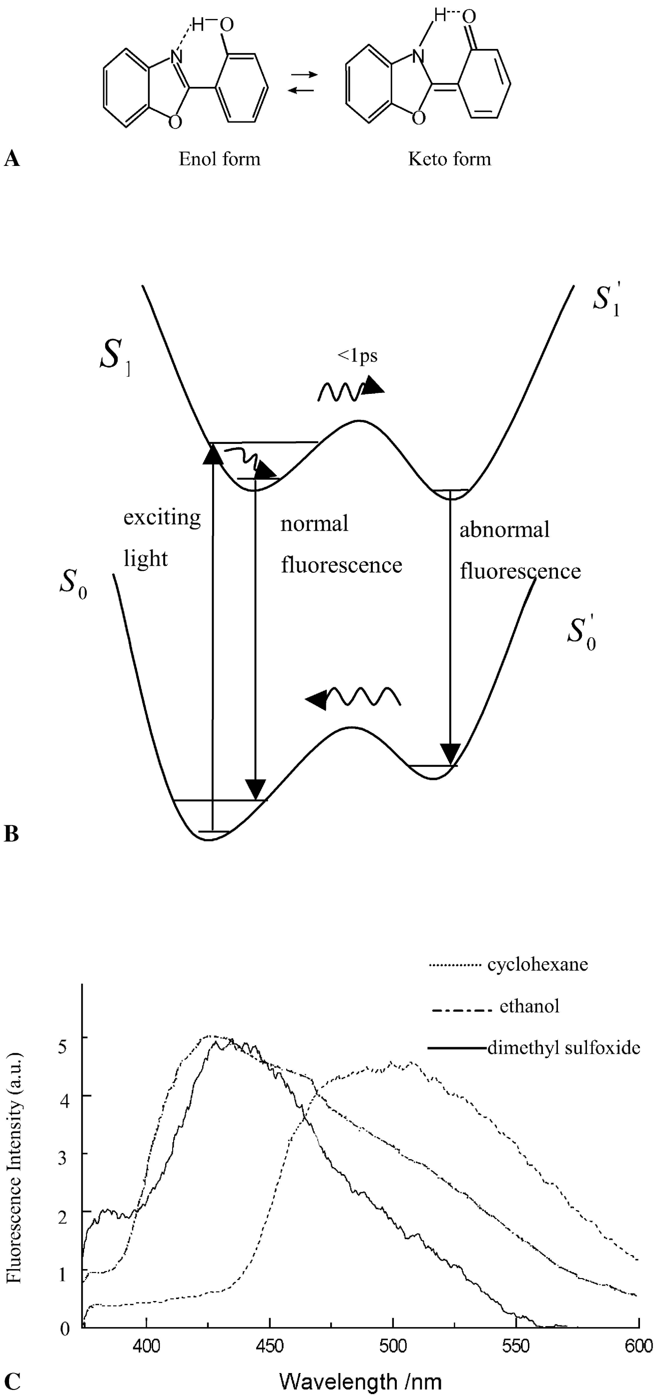

FIGURE 6 Molecular structure of HBO (**A**), potential curve of HBO with ESIPT (**B**) and fluorescence spectra of HBO in different solutions, $\lambda_{ex} = 355$ nm(**C**)

3 Discussion and conclusion

The optical switching effect of HBO originates from the deflection of the probe beam, and the latter from the change of refractive index of HBO under the irradiation of the pump beam. In this work, HBO is dissolved in three species of solvent: nonpolar solvent cyclohexane, polar solvent ethanol and strong polar solvent dimethyl sulfoxide. The nonlinear refractive index of HBO in cyclohexane is the largest among the three solvents, so that the deflection angle of the probe beam and the on–off contrast ratio of the optical switching effect are the largest for HBO in cyclohexane. The nonlinear refractive index of HBO in dimethyl sulfoxide is the smallest, so that the deflection angle of the probe beam and the on–off contrast ratio of the optical switching effect are the smallest. The situation of HBO in ethanol is the intermediate case.

In the present work, there might be two main reasons why HBO solutions exhibit a large nonlinear refractive index. One reason is the thermal effect because of absorption of the pump beam; the other reason is the ESIPT effect of HBO under the pump beam. As for the absorption of the pump beam, the extinction coefficient ε_{355} of HBO in dimethyl sulfoxide is the largest and that of HBO in ethanol is the smallest among the three solvents. This result is not consistent with the size order of the nonlinear refractive index of HBO in each solvent. Hence, the thermal effect is not the principal origin of the nonlinear refractive index of HBO. But, as for the ESIPT effect, the ESIPT efficiency of HBO in cyclohexane is the largest and that of HBO in dimethyl sulfoxide is the smallest. This result is consistent with the result of the nonlinear refractive indices of HBO in different solvents. The higher the ESIPT efficiency, the larger the nonlinear refractive index. Moreover, the refractive index of the keto form of HBO is larger than that of the enol form [15]. Thus the nonlinear refractive index of HBO is positive, as we obtained from the Z-scan curve in Fig. 5. Therefore, we conclude that the principal origin of the nonlinear refractive index of HBO is the ESIPT effect of HBO under the pump beam. The pump beam of wavelength 532 nm is beyond the region of the absorption band of HBO, so it cannot excite HBO from the ground state to the excited state, and cannot make the ESIPT process happen in HBO. Therefore, the optical switching phenomena of HBO solutions do not appear when a SHG laser (532 nm) is used as the pump beam. Why does the solvent affect the ESIPT efficiency of HBO so significantly? The reason for this will be discussed in detail elsewhere.

Because the duration of the ESIPT process is about or smaller than a picosecond and the efficiency of ESIPT is very high, an organic molecule with the ESIPT effect could be an excellent candidate material for high-speed and high-sensitivity optical switching devices.

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