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Influence of Hydrogen Bonding on the Photophysical Properties of Diethylamino Hydroxybenzoyl Hexyl Benzoate

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Abstract: In this study, we investigated the effects of different hydrogen bond types on the photophysical properties of diethylamino hydroxybenzoyl hexyl benzoate (DHHB) by systematically exploring the changes in the spectral properties of DHHB in protic and aprotic solvents. The formation and stability of hydrogen bonds were also studied, demonstrating that the system mainly existed in the form of intramolecular hydrogen bonds at low concentrations (≤5 μg/mL). In these circumstances, the fluorescent intensity, and molar absorption coefficient changed little, indicating that the intramolecular hydrogen bonds had little effect on the spectral properties of DHHB. With an increase in concentration, the number of intermolecular hydrogen bonds increased and the molar absorption coefficient significantly increased, indicating that the intermolecular hydrogen bonds were conducive to improving the UV absorption properties of DHHB. With an increase in temperature, the molar absorption coefficient of the system decreased, which reduced the UV absorption performance of DHHB. In the protic solvent, the system also contained DHHB–solvent intermolecular hydrogen bonds. With an increase in the proportion of protic solvent in the system, the fluorescent intensity of the system significantly decreased, and the UV integral area significantly increased, indicating that the hydrogen bond between DHHB and the solvent molecules was beneficial in terms of improving the UV absorption performance of DHHB.

Keywords: molecular hydrogen bonding; energy transfer; thermal motion; UV absorption properties

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1. Introduction

Diethylamino hydroxybenzoyl hexyl benzoate (DHHB) is a relatively new oil-soluble chemical sunscreen. It has a sunscreen band between 320 and 400 nm, including the entire UVA band. Due to its molecular structure being a conjugated aromatic compound containing a carbonyl group, DHHB is excited from a ground state (n) to a higher energy state (π*). As shown in Figure 1, ΔEn and ΔEp are expressed as the transition energy difference of a non-polar solvent and polar solvent, respectively. During the π–π* transition, the energy emitted is lower than the energy absorbed by the excited state at the beginning when the excited molecule returns to the ground state. This part of the energy is emitted in the form of long-wave radiation [1]. It absorbs harmful short-wave high-energy UV rays and converts the stored energy into harmless longer-wave low-energy radiation [2,3], thus playing a role in sun protection. Compared with avobenzone and other traditional high-performance UVA sunscreens, DHHB molecules contain only one C=O double bond between two benzene rings. There is no photodegradation caused by an isomerization reaction, which greatly improves photostability [4,5]. Good UV absorption, excellent light stability, and safety and environmental friendliness in water render DHHB irreplaceable in the field of sunscreen. The question of how to improve its performance has attracted the attention of many researchers in the field of cosmetics. It

is essential to explore the hydrogen bond state of molecules in sunscreen as this has a guiding significance for improvements in the UV absorption performance of sunscreen containing carbonyl-conjugated aromatic ring structures.

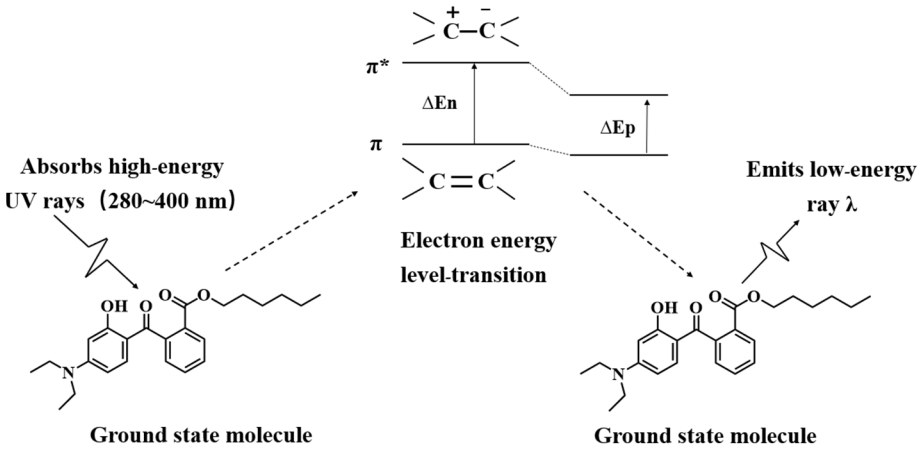

Figure 1. UV protection mechanism of DHHB.

As a special interaction force between atoms, hydrogen bonds play an important role in supramolecular chemistry, molecular recognition, photophysical chemistry, material chemistry, and catalysis [6–10]. The formation of hydrogen bonds is closely related to molecular polarity [11,12] and structure [13]. Hydrogen bonds are generally divided into intramolecular hydrogen bonds and intermolecular hydrogen bonds. Relevant studies have elaborated on the formation mechanisms of hydrogen bonds in specific compound systems. Shimada et al. [14] measured the fluorescence lifetime and quantum yield of 2′-aminophenophenone derivatives using fluorescence spectroscopy and ultraviolet absorption spectroscopy; they then studied the effects of hydrogen bond formation on the fluorescence lifetime and quantum yield. The results showed that the fluorescence lifetime and quantum yield of 2′-aminoacetophenone, 2′-(methylamino)acetophenone, and 2′-(dimethylamino)acetophenone were significantly reduced in protic solvents. The higher the hydrogen bond strength, the more significant the fluorescence quenching. This indicated that the intermolecular hydrogen bond interaction was the reason for the decrease in the fluorescence lifetime. The calculation results of the internal conversion of the photoquantum yield showed that the internal conversion of the protic solvent was significantly lower than that of the aprotic solvent, indicating that the excited-state intramolecular proton transfer reaction caused the hydrogen bond formation. Mori et al. [15] used a quantum mechanics/molecular mechanics and molecular dynamics (MD) simulation and nuclear magnetic resonance spectroscopy to study the effect of polar solvents on the hydrogen bond strength of zwitterionic hydrogen phthalate derivatives. Trajectory analysis of a methanol solution showed that the H protons tended to be close to carboxylic acid groups that formed fewer intermolecular hydrogen bonds, indicating that the formation of intermolecular hydrogen bonds was triggered by intramolecular proton transfer.

The mechanism of molecular hydrogen bond formation has been widely studied, but there are few research works on the influencing factors of hydrogen bond formation, such as temperature and concentration. In the existing literature, the characterization of hydrogen bonds has mostly been achieved using Raman spectroscopy and infrared spectroscopy. Srivastava et al. [16] simulated the effect of self-association and inter-molecular hydrogen bonds on the stretching patterns of acetonitrile and propionitrile in methanol using Raman spectroscopy and density functional theory. The outcomes demonstrated that a greater number of hydrogen bond complexes and dimers could form as the concentration of acetonitrile and propionitrile increased. Schroeder et al. [17] used an infrared thermal analysis technique to measure the hydrogen bond dissociation enthalpy of various polyamides at various temperatures to study how temperature affected the formation of

hydrogen bonds in polyamides. The results demonstrated that when the temperature rose, the intensity of the hydrogen bonds and bonding absorbance reduced. Using an infrared thermal analysis technique, Skrovanek et al. [18] investigated the effect of temperature on the hydrogen bond strength of semi-crystalline nylon PA 11. The findings demonstrated that, as the temperature increased in the N-H stretching vibration area, the strength of the hydrogen bond decreased. Due to the low sensitivity of the Raman spectrum and infrared spectrum in low-concentration systems, the majority of the related research mainly describes the hydrogen bond state in high-concentration systems through the stretching vibration intensity of the hydrogen bonds in these spectra. It is difficult to research the molecular hydrogen bond state of low-concentration systems.

Unlike intramolecular hydrogen bonds, the formation of intermolecular hydrogen bonds is closely related to the chemical environment. Intermolecular hydrogen bonds are the result of intermolecular energy transfer and are inseparable from the molecular concentration. An insufficient concentration leads to excessive molecular spacing and low energy transfer efficiency between molecules. This affects the formation of intermolecular hydrogen bonds. The stability of hydrogen bonds [19] is related to thermal motion. When the energy of the thermal motion of solvent molecules is higher than the binding energy of hydrogen bonds, the relative force of the hydrogen bonds decreases due to molecular collision, thus reducing the stability of hydrogen bonds. When the molecular concentration is high and there are enough molecules, the intermolecular hydrogen bonding force is enhanced. This is enough to resist the energy generated by the thermal motion of the solvent molecules. It is less affected by the thermal motion; therefore, additional hydrogen bonds can be generated. A low-concentration system detects fine changes in the intermolecular interaction force with greater sensitivity. This is of significance to investigations into the formation conditions of intermolecular hydrogen bonds. Our previous research observed that the detection sensitivity of ultraviolet spectroscopy and fluorescence spectroscopy in a low-concentration system was higher than that of Raman spectroscopy and infrared spectroscopy, proving their superiority for the study of molecular hydrogen bond states in low-concentration systems. The molar absorption coefficient in the ultraviolet spectrum—the characteristic constant of the tested substance—could also be used to characterize the influence of molecular hydrogen bonds on the structure, thus supplementing the study of hydrogen bond states in low-concentration systems.

Although it has been speculated that the UV absorption property of DHHB may change with changes in the structure of hydrogen bonds, there are few relevant studies on this topic, and the specific influencing factors and mechanisms remain unclear. In this study, we used ultraviolet absorption spectroscopy and fluorescence spectroscopy to investigate the effects of three protic and two aprotic solvents on the hydrogen bond formation state of DHHB and explored the formation conditions of hydrogen bonds in this system. Based on Förster's energy transfer theory, the influence of the intermolecular energy transfer distance on the hydrogen bonding force of a low-concentration system was investigated. The effect of molecular thermal motion on the stability of molecular hydrogen bonds at different temperatures was investigated using the Gibbs free energy law.

2. Materials and Methods

2.1. Experimental Materials and Instruments

2.1.1. Materials

We used methanol (Merck, Darmstadt, Germany; 99.9% purity), anhydrous ethanol (Merck; 99.9% purity), isopropyl alcohol (Fisher, Hampton, NH, USA; 99.9% purity), carbon tetrachloride (Sigma-Aldrich, St. Louis, MO, USA; 99.5% purity), n-hexane (Merck; ≥99.7% purity), and diethylamino hydroxybenzoyl hexyl benzoate (BASF CHINA LIMITED, Shanghai, China; 99% purity).

2.1.2. Instruments

We used an ultraviolet spectrophotometer (Shimadzu Instrument Company of Japan, Kyoto, Japan; UV-1800) and a fluorescence spectrophotometer (Shimadzu Instrument Company of Japan, Kyoto, Japan; RF-5301PC).

2.2. Experimental Methods

2.2.1. Preparation of the DHHB Solution

(1) DHHB solutions were prepared with different solvents (n-hexane, carbon tetrachloride, methanol, ethanol, and isopropyl alcohol) at a fixed concentration of 5 μg/mL.
(2) Different concentrations of DHHB–carbon tetrachloride solutions and DHHB–methanol solutions were prepared.

2.2.2. Ultraviolet Absorption Spectrum Test

A UV spectrophotometer was used to measure the absorbance at a scanning wavelength range of 290 nm to 450 nm and at room temperature (25 °C). According to the different concentrations of DHHB, cuvettes with different optical paths were selected, including 5 cm (0.1–0.5 μg/mL), 1 cm (1–10 μg/mL), 0.1 cm (30–100 μg/mL), and 0.015 cm (300–1000 μg/mL). A cuvette with an optical path of 0.015 cm was obtained by cutting a glass sheet with a thickness of 0.085 cm and placing it in a cuvette with an optical path of 0.1 cm.

2.2.3. Calculation of the Molar Absorption Coefficient

The molar absorption coefficient is the ability of 1 mol of the material structure to absorb ultraviolet light. Its value changes with the molecular structure. According to the ultraviolet spectrum test, we used the following formula to calculate the molar absorption coefficient (ε):

$$\varepsilon = A/CL \quad (1)$$

where A is the absorbance of the maximum absorption wavelength λmax, C is the molar concentration in mol/L, L is the thickness of the liquid layer in cm, and ε is the molar absorption coefficient in L/(mol·cm).

2.2.4. Fluorescence Spectrum Measurement

A fluorescence spectrophotometer was used to set the excitation slit and emission slit of the fluorescence spectrophotometer to 5 nm. The excitation wavelength was 377 nm, the emission wavelength was 377 nm, the scanning step size was 1 nm, and the scanning range was 390 nm~550 nm. Fluorescence scanning was performed on a solution pre-pared as per Section 2.2.1 at a temperature of 25 °C.

3. Results

3.1. Effects of Different Solvents on the Spectral Properties of DHHB

The photophysical properties of DHHB are related to whether it can form hydrogen bonds with solvents and the formed type of hydrogen bonds. As shown in Figure 2, the following three types of hydrogen bonds formed in the DHHB solution system: intramolecular hydrogen bonds of DHHB (Figure 2a), intermolecular hydrogen bonds of DHHB (Figure 2b), and intermolecular hydrogen bonds between DHHB and the solvent (Figure 2c). To explore the influence of the solvent effect of the hydrogen bond on DHHB, the concentration of DHHB was fixed at 5 μg/mL, and the aprotic solvents n-hexane and carbon tetrachloride were selected as aprotic solvent representatives. Their dielectric constants were 1.58 and 2.24, respectively. Methanol, ethanol, and isopropyl alcohol were selected as protic solvent representatives; their dielectric constants were 33.6, 24.3, and 19.92, respectively. The UV absorption spectra and fluorescence spectra were determined.

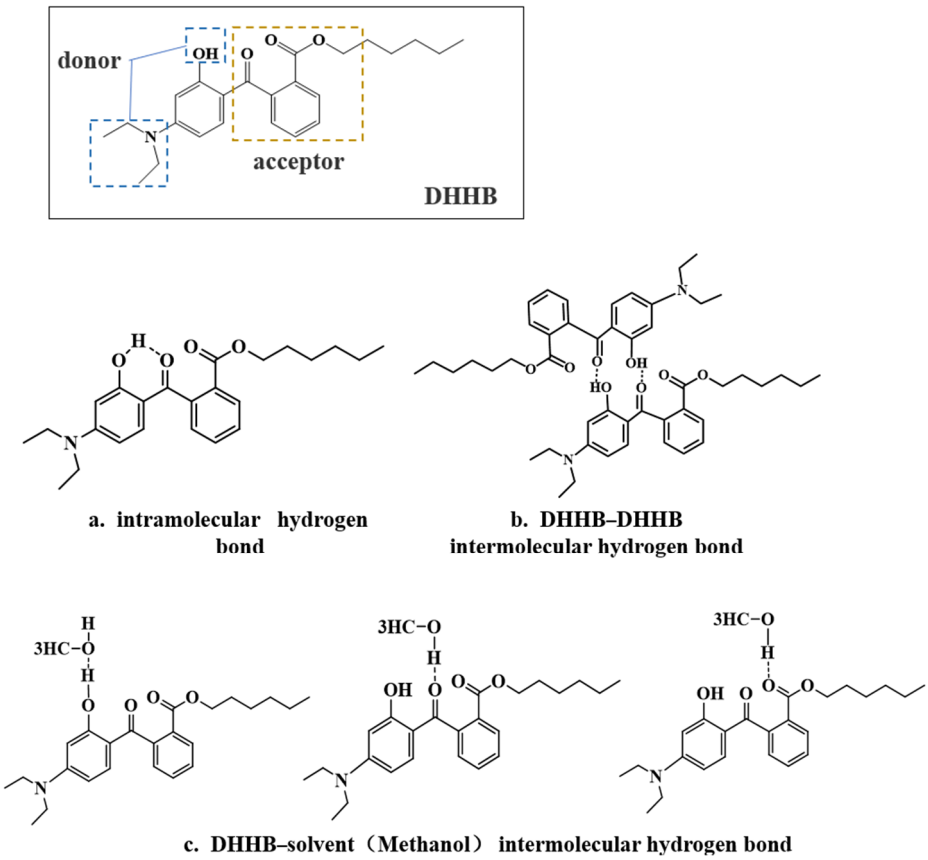

Figure 2. Molecular structure of DHHB and three hydrogen bond types.

According to our theoretical analysis, the hydrogen bond state of the DHHB molecules in aprotic solvents (n-hexane and carbon tetrachloride) was dominated by a DHHB intramolecular hydrogen bond (Figure 2a) and an intermolecular hydrogen bond (Figure 2b). Methanol, ethanol, and isopropanol were the protic solvents; their polarity and capacity to form hydrogen bonds decreased in order. The solvents could both accept and supply protons to form hydrogen bonds (Figure 2c). Therefore, all three types of hydrogen bonds existed. As shown in Figure 3, the maximum absorption wavelengths (λmax) of DHHB were 344 nm and 348 nm in n-hexane and carbon tetrachloride, respectively; λmax redshifted to 353 nm~356 nm in methanol, ethanol, and isopropanol, and the absorbance significantly increased. This phenomenon may have been a result of the formation of the P-π conjugation effect, which reduces the energy required for electrons to transition from a ground state to an excited state.

Related research [14] has shown that the formation of intermolecular hydrogen bonds in protic solvents leads to fluorescence bursts. As the ability to form hydrogen bonds increased, the quenching was more pronounced. Therefore, the fluorescence spectra of DHHB in different solvents were determined. As shown in Figure 4, the fluorescent intensity of the sample in protic solvents was lower than that in aprotic solvents. The fluorescent intensity of the DHHB molecule in carbon tetrachloride was 178; it decreased to 53, 51, and 40 in isopropanol, ethanol, and methanol, respectively. This indicated that the DHHB molecule underwent fluorescence quenching in the protic solvents and that the degree of quenching increased in turn. We speculated that the formation of molecular hydrogen bonds in protic solvents caused the excited-state molecules to release lower energy through intermolecular interactions and energy conversion, resulting in fluorescence quenching. In this process, due to a reduction in the energy of the excited-state molecules, the energy required for the electron to transition from the ground state to the excited state increased. This indicated that the λmax redshift and the intensity increase in the UV absorption spectra were due to the formation of hydrogen bonds in the structure. A

weak peak appeared at the shoulder of 460 nm in both n-hexane and carbon tetrachloride. Due to the low fluorescent intensity in n-hexane, the peak at 460 nm was not obvious; there was no such peak in the protic solvent. This may have been due to the formation of intermolecular hydrogen bonds between DHHB and the protic solvent. The 460 nm peak disappeared as a result of fluorescence quenching.

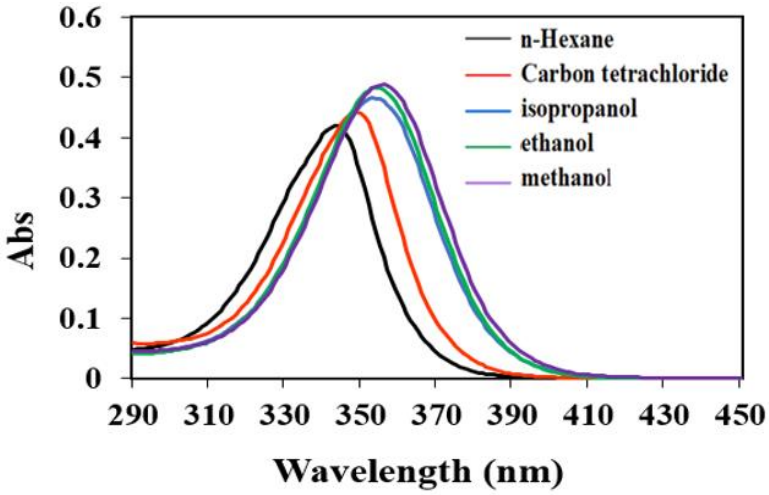

Figure 3. UV absorption spectra of 5 μg/mL DHHB in different solvents.

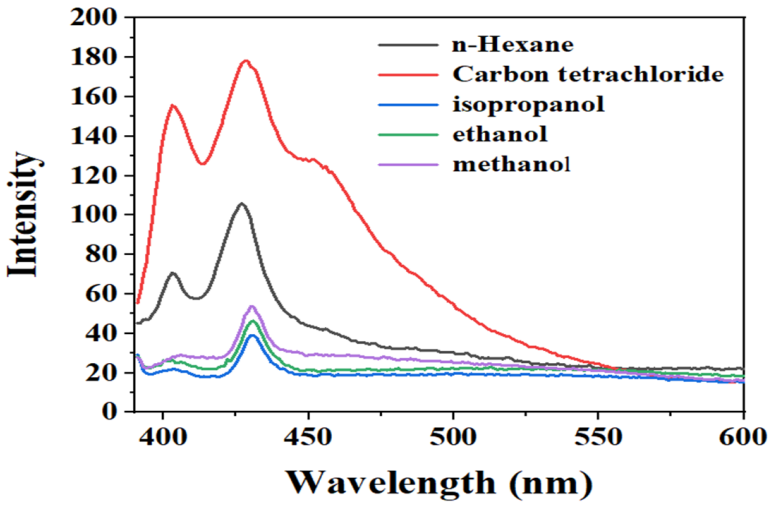

Figure 4. Fluorescence spectra of 5 μg/mL DHHB in different solvents.

3.2. The Factors Influencing DHHB Molecular Hydrogen Bonding in an Aprotic Solvent

The formation of intermolecular hydrogen bonds may be related to the distance between molecules. The intermolecular distance can be derived from the fluorescence resonance energy transfer theory [20–23]. This theory states that, in two different fluorescent groups, if the emission spectrum of one fluorescent group (the donor) overlaps with the absorption spectrum of the other group (the acceptor), a transfer of fluorescence energy from the donor to the acceptor should be observed when the distance between these two fluorescent groups is suitable. After the donor molecule is excited, when the acceptor is at a certain distance from the donor and the energy difference between the vibrational energy levels of the ground state and the first electron excited state of the donor and acceptor adapt to each other, the donor in the excited state transfers part or all of the energy to the acceptor, causing the acceptor to be excited. In this process, Förster deduced the

intermolecular distance of energy transfer from the solute concentration of the system, as shown In Formula (2):

$$C_{0L} = \frac{3}{4\pi N_A R_{0L}^3} \tag{2}$$

where N_A is Avogadr's constant, 6.022×10^{23}; C is the molar concentration, unit mol/L; and R is the intermolecular distance, Å.

Based on Forste's energy transfer theory, the intermolecular distances of DHHB at different concentrations in an aprotic solvent were calculated using Formula (2). The results are shown in Figure 5. To investigate the influence of molecular spacing on the hydrogen bond state of DHHB molecules, the UV spectrum was tested by setting different concentrations of DHHB in the aprotic solvent (carbon tetrachloride); the change in the molar absorption coefficient was then calculated.

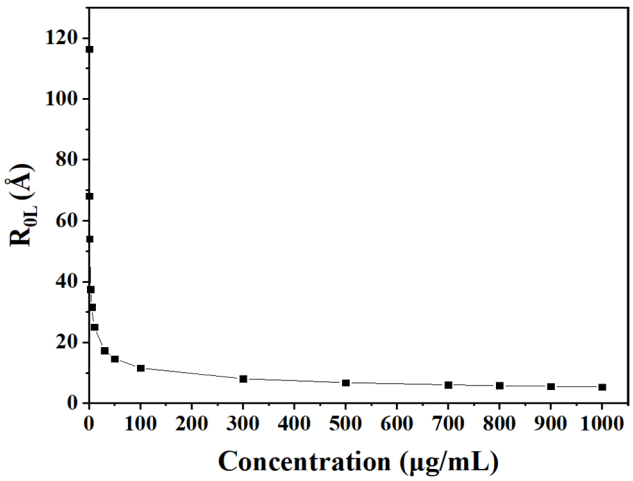

Figure 5. Molecular spacing of DHHB at different concentrations in carbon tetrachloride solution.

From Figures 5 and 6, it can be seen that, in the low-concentration range (0.1–10 μg/mL), although the intermolecular distance of DHHB rapidly decreased from 116 Å to 25 Å, the molar absorption coefficient only increased from 35,700 to 36,300. This indicated that the molecular structure change of DHHB was small. This might have been because the number of DHHB molecules at this concentration range was small and the molecular spacing was large. Therefore, the probability of a molecular collision was small, leading to the obstruction of intermolecular energy transfer. The system was dominated by intramolecular hydrogen bonds and accompanied by a small number of intermolecular hydrogen bonds. Due to the thermal motion of the molecules, the intermolecular hydrogen bonds were unstable, and the molar absorption coefficient did not significantly change. When the concentration of DHHB was in the range of 10~100 μg/mL, the intermolecular distance decreased from 25 Å to 12 Å while the molar absorption coefficient rapidly increased from 36,300 to 45,000; thus, the molecular structure of DHHB significantly changed. We speculated that, at this concentration range, the intermolecular energy transfer efficiency increased and that the energy transfer rate accelerated with the shortening of the energy transfer distance; thus, intermolecular hydrogen bonds gradually formed in the system. The formation of intermolecular hydrogen bonds enhanced the P-π conjugate effect; therefore, the molar absorption coefficient increased while the UV absorption capacity of DHHB improved. When the concentration of DHHB increased to greater than 100 μg/mL, the molecular spacing of DHHB decreased to less than 10 Å. The increase in the molar absorption coefficient slowed, which indicated that the number of intermolecular hydrogen bonds in the system had gradually reached saturation. Until the concentration of DHHB reached 700~1000 μg/mL, the molecules existed in the form of a hydrogen bond polymer association. After the molecules absorbed photons, molecular excitation energy [24] jumped between the molecules, prolonging the emission time. This resulted in the energy release of

the excited-state molecules being blocked. Therefore, the UV absorption capacity tended to be stable.

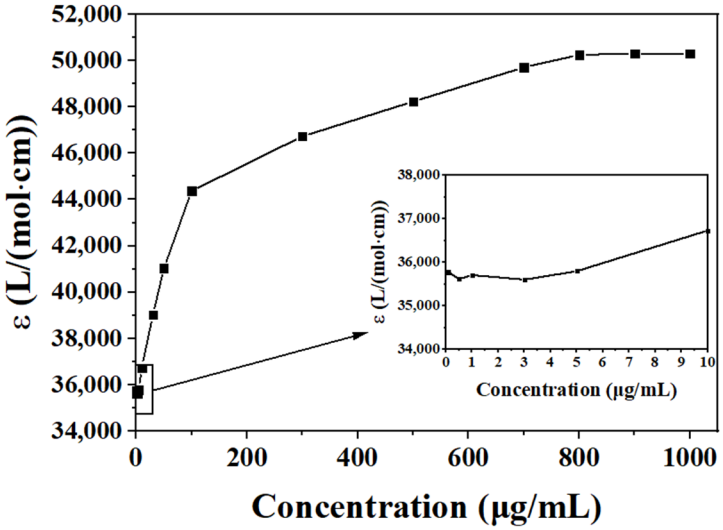

Figure 6. Molar absorption coefficient of DHHB at different concentrations in carbon tetrachloride solvent.

To verify the molecular hydrogen bonding state of DHHB at different concentrations, the changes in the fluorescent intensity of the system at different concentrations were investigated using fluorescence spectroscopy. As shown in Figure 7, when the concentration of DHHB increased to 10 μg/mL, the fluorescent intensity changed little. The fluorescent intensity significantly decreased when the concentration increased; thus, in turn, the degree of fluorescence quenching increased. When the concentration increased from 700 μg/mL to 1000 μg/mL, the fluorescent intensity decreased to almost zero. This might have been due to the vibrational relaxation of the fluorescent molecule allowing the molecule to transfer the energy of the absorbed photons to other molecules, thereby returning it to the ground state in the form of a non-radiative leap and leading to the occurrence of fluorescence quenching. When the concentration of molecules was too high, hydrogen-bonded dimers were formed between molecules, and hydrogen-bonded multimeric conjugates and intermolecular stacking occurred. This demonstrated that the formation of intermolecular hydrogen bonds was beneficial to the UV absorbance of DHHB. The formation of multimers did not significantly contribute.

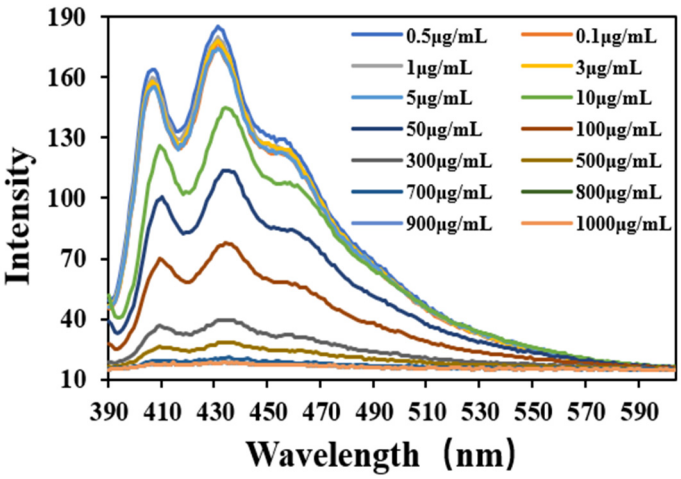

Figure 7. Fluorescence spectra of DHHB at different concentrations in carbon tetrachloride solution.

Similar to concentration, temperature is also an important factor affecting the stability of molecular hydrogen bonds. Under the effects of temperature, solvent molecules can

cause solute molecules to collide due to thermal motion [25] and exchange energy to form molecular hydrogen bonds. With an increase in the free energy of a system, the kinetic energy of thermal motion accelerates, damaging the molecular hydrogen bonds. Therefore, the variations in the molar absorption coefficients at different temperatures for different concentration systems were investigated.

Figure 8 demonstrates that the molar absorption coefficient of the system decreased with an increase in temperature at all concentrations. In the low-concentration range (≤10 μg/mL), an inflection point was observed where the molar absorption coefficient significantly increased when the concentration and temperature increased. At 4 °C, the molar absorption coefficient of the system began to increase when the concentration was higher than 3 μg/mL; this may have been due to the formation of intramolecular hydrogen bonds at this concentration. With an increase in the concentration, the molecular spacing decreased, the number of intermolecular hydrogen bonds increased, and the molar absorption coefficient gradually increased. When the temperature was increased to 25 °C and 45 °C, the inflection points of the molar absorption coefficient increased to 5 μg/mL. When the temperature was increased to 65 °C, the thermal motion significantly increased, further weakening of the stability of the intermolecular hydrogen bonds; the inflection point increased to 10 μg/mL. At temperatures of 4 °C, 25 °C, and 45 °C, the amplification of the molar absorption coefficient slowed when the concentration was higher than 100 μg/mL. When the concentration was increased to 800 μg/mL, the molar absorption coefficient tended to be stable. This indicated that the DHHB–DHHB intermolecular hydrogen bonds reached saturation after this concentration and that the molecules were stacked in the form of multipolymers. This concentration increased to 900 μg/mL when the temperature was raised to 65 °C.

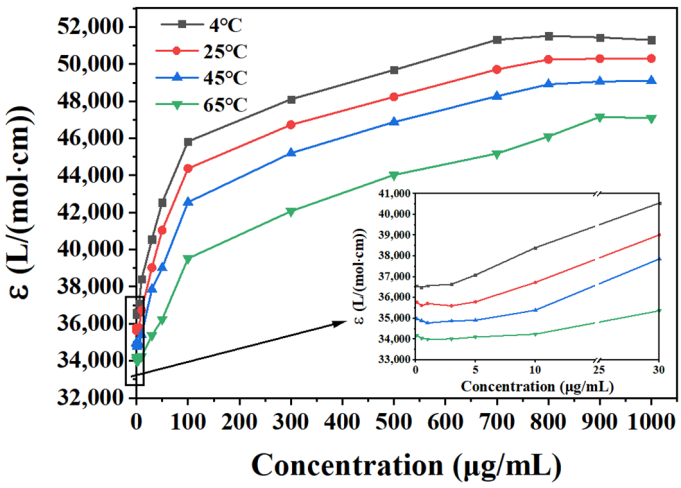

Figure 8. Molar absorption coefficient of DHHB–carbon tetrachloride at different temperatures.

The reason for this result may have been due to the collision between the thermal motion solvent molecules and the hydrogen bond. When the thermal motion energy of a solvent is greater than the hydrogen bond energy, the hydrogen bond instability is broken. After an increase in temperature, the thermal motion of a system intensifies and the free energy increases; thus, the number of stable hydrogen bonds in the system reduces [26–29]. When the temperature rises, the thermal motion of system molecules intensifies; the increase in the free energy of a system destroys the stability of the hydrogen bond [30].

3.3. The Factors Influencing DHHB Molecular Hydrogen Bonding in a Protic Solvent

To investigate the effect of heterogeneous energy transfer on the intermolecular hydrogen bonds of the solvent–DHHB, different concentrations of DHHB–methanol solutions were prepared. The effect of the molecular hydrogen bond state on the molar absorption coefficient at different DHHB concentrations was explored using UV spectrophotometry.

As shown in Figure 9, in the low-concentration range (0.1 μg/mL to 5 μg/mL), the molar absorption coefficient of the system slowly increased. The increased rate was higher than that of the DHHB–carbon tetrachloride system. This may have been due to the formation of intermolecular hydrogen bonds between the methanol and DHHB molecules. When the concentration of DHHB increased from 5 μg/mL to 100 μg/mL, the molar absorption coefficient significantly increased. When the concentration of DHHB was greater than 100 μg/mL, the increase in the molar absorption coefficient slowed until it reached equilibrium. This result was mainly due to the formation of hydrogen bonds between the methanol and DHHB molecules in the methanol solvent, which accelerated the saturation of hydrogen bonds in the system. This indicated that the formation of solvent–DHHB intermolecular hydrogen bonds could improve the UV absorption of DHHB.

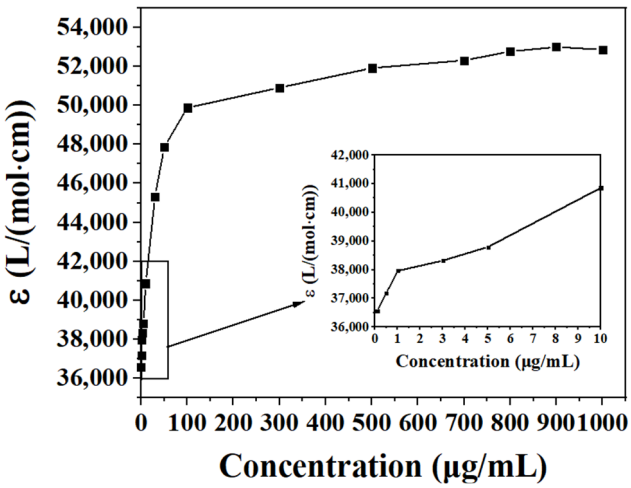

Figure 9. Molar absorption coefficient of DHHB at different concentrations in methanol.

To investigate the effect of the ratio of solvent–DHHB intermolecular hydrogen bonds on the UV absorption performance of DHHB, the concentration of DHHB was fixed at 5 μg/mL, and the UV absorption spectra of the system were investigated under different volume ratios of aprotic solvent (carbon tetrachloride) to protic solvent (methanol). By calculating the integral area of the UVA band (320~400 nm), the influence of the hydrogen bond type on the UV absorption performance of DHHB was analyzed.

Figure 10 demonstrates that, as the volume fraction of methanol increased, the maximum absorption wavelength of the system shifted to red; thus, in turn, the maximum absorbance increased. When the volume ratio reached 3:7, the absorbance curves did not significantly change. With a continual increase in the volume of methanol, a high degree of overlap occurred. The integrated area of the UVA region significantly increased when the volume fraction of methanol increased from 0 to 20%, as shown in Figure 11. This might have been due to the gradual formation of hydrogen bonds between the methanol–DHHB molecules. With an increase in the volume fraction of methanol, the increase in the integral area began to slow down. This may have contributed to the number of free DHHB molecules that could form intermolecular hydrogen bonds with the solvent molecules, which decreased as the volume of protic solvent increased at a fixed DHHB concentration. When the volume fraction of methanol was increased to 70%, the integrated area effectively reached equilibrium; thus, we assumed that the methanol–DHHB intermolecular hydrogen bonds had reached saturation. This demonstrated that the formation of solvent–DHHB intermolecular hydrogen bonds was beneficial to improving the UV absorption performance of DHHB.

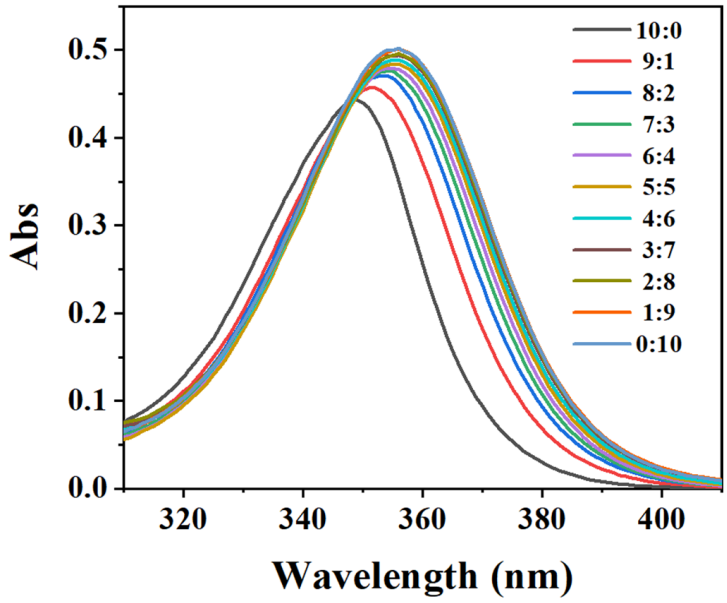

Figure 10. UV spectra of DHHB solutions at different carbon tetrachloride/methanol volume ratios.

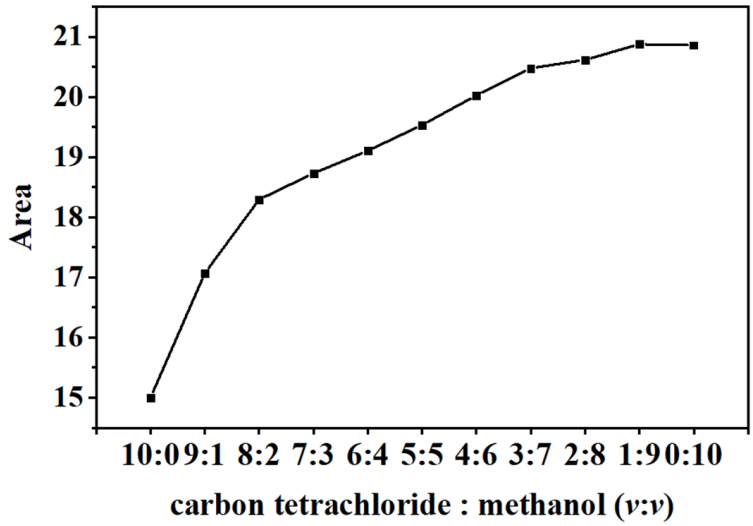

Figure 11. Integrated area of UVA region of DHHB solution at different carbon tetrachloride/methanol volume ratios.

The change in the hydrogen bond state of the DHHB molecules under different volume fractions was verified by using fluorescence spectroscopy. As shown in Figure 12, the fluorescent intensity of the system rapidly decreased from 187 to 87 as the volume fraction of methanol increased from 0 to 20%. This indicated that the number of solvent–DHHB intermolecular hydrogen bonds in the system had rapidly increased. When the volume fraction of methanol increased to 70%, the fluorescent intensity decreased to 49, indicating that the number of hydrogen bonds between the solvent and DHHB molecules had gradually reached saturation in this process. When the methanol volume fraction increased, the fluorescent intensity changed slightly. The experimental results were consistent with the integrated area results, verifying that the methanol–DHHB molecular hydrogen bond was beneficial to enhancing the UV absorption performance of DHHB.

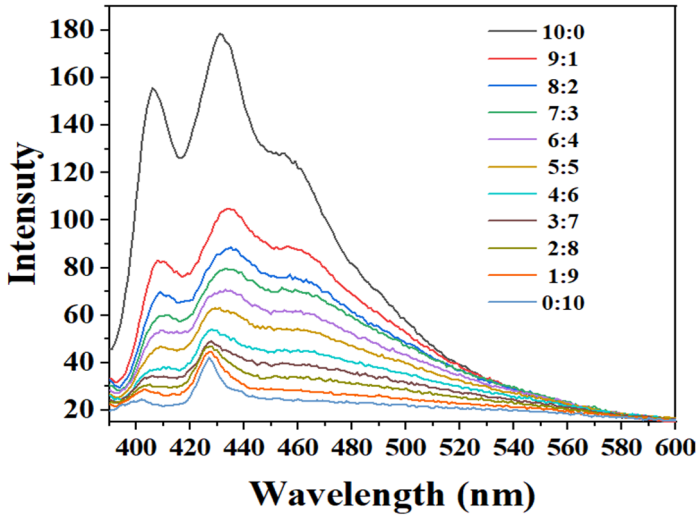

Figure 12. Fluorescence spectra of DHHB solution at different carbon tetrachloride/methanol volume ratios.

4. Conclusions

The effects of molecular hydrogen bonds on the UV absorption properties of DHHB were investigated by measuring the UV spectra and fluorescence spectra of DHHB in different protic and aprotic solvents. The effect of the intermolecular energy transfer distance on the formation of hydrogen bonds at different concentrations was investigated by measuring the molar absorption coefficient of DHHB at different concentrations in carbon tetrachloride and methanol solutions. The results demonstrated that, at a low concentration ($\leq$ 5 μg/mL), the probability of intermolecular collision was small due to the concentration of the system being diluted enough. The intermolecular distance was large, thereby reducing the efficiency of intermolecular energy transfer; the system mainly formed intramolecular hydrogen bonds. The intermolecular hydrogen bonds formed in the system may have been unstable due to the collision of thermally moving molecules. As the concentration increased, the number of stable intermolecular hydrogen bonds increased. The molar absorption coefficient did not significantly increase when increasing the concentration of DHHB. This indicated that, when the concentration of DHHB increased to a certain extent, the intermolecular hydrogen bonds reached saturation, prompting the system to form hydrogen bond dimers and multimolecular associations.

The change in the molar absorption coefficient of DHHB at different temperatures and different concentrations was investigated. The influence of temperature on the stability of the hydrogen bond was probably because the energy from the thermal motion of the solvent molecules was greater than the energy of the hydrogen bond, which caused the hydrogen bond to break after collision. As the temperature increased, the molecular thermal motion intensified while the free energy of the system increased, which was not conducive to the stability of the intermolecular hydrogen bonds. This reduced the UV absorption performance of DHHB.

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References

1. Shaath, N.A. On the theory of ultraviolet absorption by sunscreen chemicals. *J. Soc. Cosmet. Chem.* **1987**, *82*, 193–207.
2. Grbovi, G.; Malev, O.; Dolenc, D.; Klobučar, R.S.; Cvetković, Z.; Cvetković, B.; Jovančićević, B.; Trebše, P. Synthesis, characterisation and aquatic ecotoxicity of the UV filter hexyl 2-(4-diethylamino-2-hydroxybenzoyl)benzoate (DHHB) and its chlorinated by-products. *Environ. Chem.* **2016**, *13*, 119–126. [CrossRef]
3. Kao, M.H.; Venkatraman, R.K.; Sneha, M.; Wilton, M.; Orr-Ewing, A.J. Influence of the Solvent Environment on the Ultrafast Relaxation Pathways of a Sunscreen Molecule Diethylamino Hydroxybenzoyl Hexyl Benzoate. *J. Phys. Chem. A* **2021**, *125*, 636–645. [CrossRef] [PubMed]
4. Sohn, M.; Baptiste, L.; Quass, K.; Settels, V.; Herzog, B. Photokinetics of oil soluble 1,3,5-Triazine UV filters in combination with Butyl Methoxydibenzoylmethane or with Diethylamino Hydroxybenzoyl Hexyl Benzoate. *J. Photochem. Photobiol.* **2021**, *8*, 100073. [CrossRef]
5. Kawakami, C.M.; Máximo, L.N.C.; Fontanezi, B.B.; da Silva, R.S.; Gaspar, L.R. Diethylamino hydroxybenzoyl hexyl benzoate (DHHB) as additive to the UV filter avobenzone in cosmetic sunscreen formulations-Evaluation of the photochemical behavior and photostabilizing effect. *Eur. J. Pharm. Sci.* **2017**, *99*, 299–309. [CrossRef]
6. Biswakarma, J.J.; Ciocoi, V.; Topper, R.Q. Energetics, Thermodynamics, and Hydrogen Bonding Diversity in Ammonium Halide Clusters. *J. Phys. Chem. A* **2016**, *120*, 7924–7934. [CrossRef]
7. Chan, B.; Easton, C.J.; Radom, L. Effect of Hydrogen Bonding and Partial Deprotonation on the Oxidation of Peptides. *J. Phys. Chem. A* **2018**, *122*, 1741–1746. [CrossRef]
8. Iwata, T.; Nagai, T.; Ito, S.; Osoegawa, S.; Iseki, M.; Watanabe, M.; Unno, M.; Kitagawa, S.; Kandori, H. Hydrogen Bonding Environments in the Photocycle Process around the Flavin Chromophore of the AppA-BLUF domain. *J. Am. Chem. Soc.* **2018**, *140*, 11982–11991. [CrossRef]
9. Rawat, P.; Singh, R.N. Evaluation of molecular assembly, spectroscopic interpretation, intra-/inter molecular hydrogen bonding and chemical reactivity of two pyrrole precursors. *J. Mol. Struct.* **2014**, *1075*, 462–470. [CrossRef]
10. Piskulich, Z.A.; Laage, D.; Thompson, W.H. On the role of hydrogen-bond exchanges in the spectral diffusion of water. *J. Chem. Phys.* **2021**, *154*, 064501. [CrossRef]
11. Motin, M.A.; Mia, M.A.H.; Islam, A.K.M.N. Thermodynamic properties of Sodium Dodecyl Sulfate aqueous solutions with Methanol, Ethanol, n-Propanol and iso-Propanol at different temperatures. *J. Saudi Chem. Soc.* **2015**, *19*, 172–180. [CrossRef]
12. Satheesh, B.; Sreenu, D.; Chandrasekhar, M.; Jyostna, T.S. Interpretation of hydrogen bonding formation through thermodynamic, spectroscopic and DFT studies between isoamyl alcohol and benzyl alcohol at T = (293.15 to 318.15) K. *J. Mol. Liq.* **2020**, *317*, 113942. [CrossRef]
13. Wang, X.P.; Yang, F.X.; Gao, Y.; Liu, Z.J. Volumetric properties of binary mixtures of dimethyl sulfoxide with amines from (293.15 to 363.15) K. *J. Chem. Thermodyn.* **2013**, *57*, 145–151. [CrossRef]
14. Shimada, H.; Nakamura, A.; Yoshihara, T.; Tobita, S. Intramolecular and intermolecular hydrogen-bonding effects on photophysical properties of 2′-aminoacetophenone and its derivatives in solution. *Photochem. Photobiol. Sci. Off. J. Eur. Photochem. Assoc. Eur. Soc. Photobiol.* **2005**, *4*, 367–375. [CrossRef]
15. Mori, Y.; Masuda, Y. Effect of solvent on proton location and dynamic behavior in short intramolecular hydrogen bonds studied by molecular dynamics simulations and NMR experiments. *Chem. Phys.* **2015**, *458*, 18–29. [CrossRef]
16. Srivastava, S.K.; Ojha, A.K.; Raghuvansh, P. Influence of self-association and inter-molecular hydrogen bonding on the ν(C≡N) stretching mode of CH3C≡N and C2H5C≡N in binary mixtures with CH3OH—A comparative study via concentration-dependent polarized Raman study and ab initio calculation. *J. Raman Spectrosc.* **2006**, *37*, 1287–1295. [CrossRef]
17. Schroeder, L.R.; Cooper, S.L. Hydrogen bonding in polyamides. *J. Appl. Phys.* **1976**, *47*, 4310–4317. [CrossRef]
18. Skrovanek, D.J.; Painter, P.C.; Coleman, M.M. Hydrogen bonding in polymers. 2. Infrared temperature studies of nylon 11. *Macromolecules* **1986**, *19*, 699–705. [CrossRef]
19. Masae, T.; Hiroshi, M.; Yuka, I. Assessment of the VDW interaction converting DMAPS from the thermal-motion form to the hydrogen-bonded form. *Sci. Rep.* **2019**, *9*, 13104–13113.
20. Medintz, I.; Hildebrandt, N. *FRET-Förster Resonance Energy Transfer: From Theory to Applications*; Wiley-VCH Verlag GmbH: Weinheim, Germany, 2013.
21. Foster, T.H.; Foster, V. Zwischenmolekulare Energiewanderung und Fluoreszenz. *Ann. Phys.* **1948**, *2*, 55–75. [CrossRef]
22. Harms, G.; Wild, U. Time-resolved fluorescence study on the mechanism of polarizing energy transfer in uniaxially oriented polymer blends. *Phys. Chem. Chem. Phys.* **1999**, *1*, 5697–5702.
23. Sadananda, M.; Miguel, G.I.; Mine, I. Photoinduced Energy Transfer in ZnCdSeS Quantum Dot–Phthalocyanines Hybrids. *ACS Omega* **2018**, *3*, 10048–10057.

24. Shrivastava, R. Near White Light Emission and Concentration Quenching of Calcium Titanate Doped with Dysprosium (III) Phosphors. *J. Fluoresc.* **2019**, *29*, 369–374. [CrossRef] [PubMed]
25. Akiva, A.; Chuntonov, L. Intramolecular hydrogen bonding protects the hydroxyl group from attack by fluctuating solvent forces. *J. Chem. Phys.* **2020**, *152*, 074502. [CrossRef] [PubMed]
26. Piskulich, Z.A.; Laage, D.; Thompson, W.H. Activation energies and the extended jump model: How temperature affects reorientation and hydrogen-bond exchange dynamics in water. *J. Chem. Phys.* **2020**, *153*, 074110. [CrossRef]
27. Walker, J.S.; Vause, C.A. Reappearing Phases. *Sci. Am.* **1987**, *256*, 98–105. [CrossRef]
28. Brink, G.; Glasser, L. Studies in hydrogen bonding: The enthalpy of hydrogen bond formation of ethanol in carbon tetrachloride solutions. *J. Mol. Struct.* **1986**, *145*, 219–224. [CrossRef]
29. Zhao, G.J.; Liu, J.Y.; Zhou, L.C. Site-selective photoinduced electron transfer from alcoholic solvents to the chromophore facilitated by hydrogen bonding: A new fluorescence quenching mechanism. *J. Phys. Chem. B* **2007**, *111*, 8940–8945. [CrossRef]
30. Zelig, C.; Yoav, T. Hydrogen bonding of dimethylpyridine clusters in water: Correlation between the lower consolute solution temperature and electron interaction energy. *J. Chem. Phys.* **2020**, *152*, 204304.

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