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A Study of Competitive Multiple Hydrogen Bonding Effect and Its Associated Excited-State Proton Transfer Tautomerism

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1,8-Dihydroxynaphthalene-2,7-dicarbaldehyde (DHDA) has been strategically designed and synthesized in a aim to study the competitive multiple hydrogen bonding (H-bonding) effect and the associated excited-state intramolecular proton transfer reaction (ESIPT). In nonpolar solvents such as cyclohexane, equilibrium exists between two H-bonding isomers DHDA-23_00 and DHDA-23_0I (Scheme 1), which all possess double intramolecular H-bonds. In polar, aprotic solvents such as CH₂Cl₂, DHDA-23 OO becomes the predominant species. Due to various degrees of H-bond induced changes of electronic configuration each isomer reveals distinct absorption feature and excited-state behavior, in which DHDA-23 OI in cyclohexane undergoes double ESIPT in a stepwise manner, giving the first and second proton-transfer tautomer emissions maximized at ~500 nm and 660 nm, respectively. As for DHDA-23_00 both single and double ESIPT are prohibited, resulting in an intense normal 450 nm emission band. In a single crystal DHDA-23_0I is the dominant species, which undergoes excited state double proton transfer, giving intense 530 nm and 650 nm emission bands. The mechanism associated with competitive multiple H-bonding energetics and ESIPT was underpinned by detailed spectroscopy/dynamics and computational approaches.

1. Introduction

Recently, excited-state intramolecular proton transfer (ESIPT) involving multiple protons has been attracting considerable attention.¹⁻⁶ On the one hand, it offers the opportunity to mimic the ubiquitous proton transfer phenomena in biological systems⁷⁻¹¹ that incorporating moving multiple protons across bridging hydrogen bond (H-bond). On the other hand, from viewpoint of lighting and display, multiple ESIPT may consequently lead to multiple emission bands that warrant white light generation with a single type of molecule.¹²⁻¹⁴ However, probing the mechanism of multiple proton transfer, including the energetics of reaction pathways, the simultaneous proton transfer versus stepwise relocation, etc., is challenging because the structures of the intermediates could be ill-defined, particularly when environment perturbations are also involved.^{1-5,10, 15, 16}

Very recently, we have judiciously designed a molecule 1,8dihydroxy-2-naphthaldehyde (DHNA, see Scheme 1a) that shows a distinct stepwise double proton transfer in the excited state¹⁷. Upon UV electronic excitation, two large Stokes shifted emission bands maximized at 520 nm and 650 nm are resolved, which are ascribed to the tautomer emission resulting from the first and second proton transfer products, denoted by TA* and TB* respectively (see Scheme 1(a), * denotes the excited state). The first proton transfer $(DHNA^* \rightarrow TA^*)$ is ultrafast (< system response of 150 fs), while the second proton transfer is reversible, for which the rates of forward (TA* \rightarrow TB*) and backward (TA* \leftarrow TB*) proton transfer were determined to be $(1.7 \text{ ps})^{-1}$ and $(3.6 \text{ ps})^{-1}$ $(ps)^{-1}$, respectively. The fast equilibrium leads to identical population lifetimes of ~54 ps for both TA* and TB* tautomers. Thus, the napthaldahyde molecule provides valuable fundamental insight into the multiple ESIPT reaction.

In an aim to gain more insight into the single versus double excited-state intramolecular proton transfer, in this study, we synthesized a new DHNA derivative, namely 1,8dihydroxynaphthalene-2,7-dicarbaldehyde (DHDA, see Scheme 1b). Similar to DHNA, DHDA is expected to form two intramolecular H-bonds free from intermolecular H-bond perturbation.^{18, 19} The difference, however, lies in the existence of different types of H-bond conformers. For example, shown in Scheme 1(b), the H-bond isomer DHDA-23_OI possesses C=O(1)---HO(2)---HO(3) sequential dual Hbonds while the other isomer DHDA-23_OO consists of a pair of C=O(1 or 4)---HO(2 or 3) symmetric H-bonds. Various degrees of H-bond strength and position are expected to have distinctive electron distribution and hence different photophysical properties for various DHDA isomers. Scheme 1(b) also depicts the possible proton-transfer tautomer



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structures under the occurrence of first and second ESIPT for **DHDA-23_OI** and **DHDA-23_OO** without energetic concerns. Details of ground-state isomerization and excited-state single versus double proton transfer are elaborated in the following sections.



Scheme 1. (a) Structure of **DHNA** and its associated proton transfer reaction.¹⁷ (b) Two proposed dual H-bonded structures of aldehyde **DHDA** and their possible proton-transfer isomers after single and double ESIPT reaction.

2. Results and discussion

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2.1 Syntheses and Structural Characterization

Compound **DHDA** was prepared from naphthalene-1,8-diol (1) following the literature ^{17, 20, 21} (Scheme 2). In brief, **1** was reacted with NaH and chloromethyl ethyl ether by protecting the hydroxyl protons to form 1,8-bis(ethoxymethoxy)naphthalene (2). The addition of the aldehyde group on **2**, forming 1,8-bis(ethoxymethoxy)naphthalene-2,7-dicarbaldehyde (**3**), was accomplished using n-BuLi and tetramethylethylenediamine (TMEDA), followed by addition of two stoichiometric DMF. Deprotection of **3** under an acid condition gave **DHDA** in 75% yield (see supporting information for detailed synthetic methods and Figures S1-S4 for characterization).

Scheme 2. The synthetic routes of DHDA and the structure of HN and HMN.



Figure 1 depicts the single crystal structure and the packing of **DHDA** in the unit cell. Monoclinic **DHDA** single crystals belong to the space group of P2(1)/n, with cell parameters of a = 3.7960(3) Å, b = 18.3816(13) Å, c = 13.3342(10) Å, $\alpha = \gamma = 90^{\circ}$, and $\beta = 90.367(5)^{\circ}$ (see Tables S1~S3 and Fig. S1 in detail). According to Fig. 1(a), the hydrogen bonds of **DHDA** are asymmetric. The distances between two hydrogen bonds of O(2)H····O(1) and O(3)H····O(2) are estimated to be 1.78 and 1.90 Å, respectively, strongly supporting the existence of dual intramolecular hydrogen bonds in the crystalline.

In solvents such as CDCl₃, the ¹H-NMR spectrum of **DHDA** (see Fig. S2) exhibits one relatively broad peak at 12.6 ppm and the other sharp peak at 10.1 ppm, which is assigned to the -OH and CHO protons, respectively. This assignment is supported by the computational approach (vide infra) as well as the comparison with the controlled compound, 1-hydroxy-8-methoxy-2-naphthaldehyde (HN, see Scheme 2) which reveals two proton peaks at 12.6 and 9.9 ppm (Fig. S3) and are unambiguously assigned to -OH and CHO protons, respectively. The results manifest two symmetric Hbonding sites for DHDA in CDCl₃, which is in sharp contrast to the asymmetric O(2)H···O(1) and O(3)H···O(2) H-bonds in crystal. The difference of H-bond configuration between solution and solid lies in the strong polar-polar intermolecular HC=O(4) ··· HC=O(4) interaction in the DHDA crystal, which reveals an intermolecular C(12)H(12)O(4)···H(11)O(1)C(11) distance of 2.62 Å between two vicinal monomers (see Fig. 1 (b), green dashed line), constructing a zigzag chain parallel to the b axis direction. Such a crystal packing makes the CH(12)O(4) group slightly twisted out of the naphthalene plane without involvement on intramolecular H-bonds.



Figure 1. (a) The X-ray structure of DHDA thermal ellipsoids drawn at 50% probability level. (b) View of the packing of DHDA in the unit cell.

2.2 Photophysical study in solution

As shown in Fig. 2, **DHDA** exhibits the lowest lying absorption band maximized at 400 nm ($\varepsilon^{-1.1} \times 10^4$ M⁻¹cm⁻¹), which is reasonably attributed to a $\pi\pi^*$ transition. Upon electronic excitation, **DHDA** clearly exhibits a dominant emission band maximized at 445 nm in cyclohexane, accompanied by a small, large Stokes shifted emission maximum at 660 nm (Fig. 2). Upon monitoring at the 450 nm and 650 nm emission regions, the respective excitation spectra are slightly different, in which the excitation spectrum monitored at 450 nm emission shows a characteristic vibronic progression with a peak at 400 nm and an onset at ~430 nm, while that for 660 nm shows less structural feature with the onset being red shifted to

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500 nm. Moreover, upon excitation at e.g. 440 nm, bypassing the onset of the 400 nm excitation spectral band, weak dual emission bands maximized at 505 nm and 660 nm were resolved (see inset of Fig. 2). Upon dissolving **DHDA** in polar solvents such as CH_2Cl_2 and CH_3CN . The emission character in CH_2Cl_2 is similar to that in cyclohexane, but the 660 nm intensity is much decreased. In highly polar solvent such as CH_3CN , we observed solely the 480 nm emission band and no emission bands at ~510 and 660 nm could be resolved (see Fig. S5). The solvent polarity dependence in spectral changes is reversible, indicating that the multiple emission bands observed in cyclohexane are not from impurity but an intrinsic property.

According to the above steady state spectroscopy, DHDA in nonpolar solvents clearly exist at least two types of H-bonding isomers, tentatively assigned to be DHDA-23_00 and DHDA-23_0I (Scheme 1(b)) in the ground state, in which the major isomer, upon excitation, gives rise to normal 450 nm emission, while the minor populated isomer exhibits both 510 nm and 660 nm emissions. Increasing the solvent polarity leads to prevailing population of DHDA-23_00. Prior to the structural assignment, it is noteworthy that the proposed DHDA-23_OI isomer possesses the same dual Hbonding sites as DHNA (cf. Scheme 1(a)). Therefore, it is reasonable to assume that similar to DHNA,¹⁷ DHDA-23_OI undergoes stepwise double proton transfer in the excited state, resulting in DHDA-13 II* and DHDA-12 II* isomers (see Scheme 1(b)), which exhibit ~500 nm and 660 nm emission bands, respectively (see inset of Fig. 2). The other conformer DHDA-23 OO possesses a pair of C=O---HO symmetric H-bonds and is the predominant species in polar solvent such as CDCl₃ according to ¹H-NMR results (vide supra). DHDA-23_00 exhibits only normal 445 nm emission, for which the emission spectral feature and peak wavelength are similar to that of non-ESIPT compound 3 (see Scheme 2 and Fig. S6). Accordingly, both single and double proton transfers are prohibited for DHDA-23_00.



Figure 2. Absorption (black), emission (dotted black, excited at 380 nm) and excitation (monitored at 450 nm (red) and 660 nm (blue) emissions) spectra of **DHDA**. Inset: the enlarged emission at 660 nm (black, λ_{ex} = 380 nm) and the emission at > 500 nm (green, λ_{ex} = 440 nm).

Despite having double intramolecular H-bonds, the prohibition of ESIPT for DHDA-23_00 is uncommon, which is of fundamental interest to shed light on its H-bond/ESIPT relationship. First, we notice that 1-hydroxyl-2-naphthaldehyde (**HN**, scheme 2), which possesses a single O-H---O=CH H-bond, exhibits both normal and proton-transfer tautomer emissions due to the existence of thermal equilibrium between normal and tautomer in the excited states.²²

Therefore, it is reasonable that the excited-state equilibrium would be perturbed via substituent effect of HN. On this basis, we then examined the derivative HN, namely HMN (Scheme 2), which possesses an O-H---O=C H-bond, supported by the ¹H-NMR (Fig. S3). As shown in Fig. S7, HMN in cyclohexane exhibits only one emission band maximized at 450 nm that is unambiguously assigned to the normal emission. Therefore, for HMN that mimics the single Hbonding site of DHDA-23 OO isomer, a single proton transfer in the excited state seems to be thermally inaccessible. Likewise, it is reasonable for us to propose that single proton transfer is prohibited in DHDA-23 OO. The result further infers that stepwise double proton transfer cannot take place in DHDA-23 OO. On the other hand, our computational approach elaborated in the later section (vide infra) also concludes that concerted double proton transfer in DHDA-23 OO is highly endergonic. Both viewpoints support the experimental results that only normal emission was observed for DHDA-23_00.

We then made attempts to further resolve the dynamics of ESIPT for DHDA by using the femtosecond fluorescence upconversion technique. A typical result in cyclohexane is shown in Fig. 3 while the pertinent data are listed in Table 1. Upon 400 nm excitation and monitoring at the blue emission region of e.g. 460 nm, the fluorescence upconverted signal clearly reveals dual decay components, consisting of an ultrafast system-response (~150 fs) decay and a much longer population decay component that was further resolved to be 788±15 ps by the time-correlated single photon counting (TCSPC) measurement. In accordance with the steady state emission the long 788 ps decay component can reasonably be assigned to the population decay from the symmetric DHDA-23_OO conformer, for which ESIPT is prohibited (vide supra). On the other hand, the emission monitored at e.g. 650 nm consists of a 1.1±0.3 ps rise component and a decay time of 35±3.2 ps (Fig. 3 and Table 1). The rise component (1.1 ps) of the emission at 650 nm is well-matched with the decay component (1.1 ps) of emission monitored at 520 nm upon 420 nm excitation. Another result worth to note is the identical population decay times for both 520 and 650 nm emission bands (~35 ps), indicating equilibrium between two excited-state species. This, together with the an ultrafast decay component (< 150 fs) monitoring at 460 nm emission (vide supra), is reminiscent of the ESIPT mechanism of DHNA.¹⁷ Therefore, similar to DHNA, a stepwise double proton transfer takes place in DHDA-23_OI where upon excitation a < 150 fs single proton transfer takes place, forming DHDA-13_II*, followed by second proton transfer to DHDA-12 II*. DHDA-13 II* and DHDA-12 II* are in fast equilibrium, giving 505 nm and 660 nm emission bands, respectively, with identical population decay time of 35 ps. The result clearly leads to the conclusion of the precursor (DHDA-12 II*)-successor (DHDA-13_II*) reversible type proton-transfer relationship. As a result, the equilibrium constant $K_{eq} = k_{pt2}/k_{-pt2}$ (Scheme 3, see SI for derivation) can be obtained by the ratio of the pre-exponential factor at t = 0, which is deduced to be 4.72 (see Fig. 2), corresponding to a ΔG of -0.92 kcal/mol from DHDA-13_II* to DHDA-12 II*. The forward and backward proton transfer rate constants can be further deduced to be $k_{pt2} = (1.3 \text{ ps})^{-1}$ and $k_{-pt2} =$ (6.3 ps)⁻¹. Lastly, despite the ground-state equilibrium between

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Compounds (solvent)	observed λ_{abs}/nm (ϵ /M ⁻¹ cm ⁻¹)	λ_{monitor} / nm	Q.Y /%	τ_{obs} (pre-exponential factor)
DHDA (cyclohexane)	400 (11000)	460 520 650	9.4	<150 fs ^a (0.40), 788± 15 ps ^b (0.60) 1.1 ± 0.2 ps ^a (0.74); 34 ± 3.6 ps ^{a,b} (0.16); 788 ± 13 (0.10) 1.1 ± 0.3ps ^a (-0.25); 35 ± 3.2 ps ^{a,b} (0.75)
DHDA (solid)	-	520 700	4.9	134 ±5 ps ^b 139 ± 5 ps ^b

^{a.} The lifetime was measured using an ultrafast fluorescence up-conversion technique.

^{b.} Lifetime was measured by a TCSPC system with femtosecond excitation pulses.

^{c.} Lifetime was measured by a TCSPC system with a pulsed hydrogen-filled lamp as the excitation source.

DHDA-23_OO and DHDA-23_OI their interconversion does not 2.3 Excited-state double proton transfer in single crystal take place during the excited-state life span (see Scheme 3).

Table 1. The photophysical properties of DHDA



Figure 3. Time-resolved femtosecond fluorescence up-conversion of DHDA in cyclohexane monitored at (a) 460 nm, (b) 520 nm and (c) 650 nm. Solid red lines depict the corresponding fitting curves. λ_{ex} = 400 nm for (a) and (c), λ_{ex} = 420 nm for (b).



Scheme 3. The proposed double proton transfer model for DHDA in cvclohexane.

We also performed spectroscopy and dynamics measurement in a single crystal in an attempt to make a direct correlation with the molecular structure. The x-ray disclosed crystal structure of DHDA to be solely in the DHDA-23_OI isomer. Therefore, we expect that the ESIPT dynamics, if there is any, should be similar to that observed in the **DHNA** crystal¹⁴. As a result, the emission of **DHDA** in the single crystal showed a dual emission maximized at 530 nm and 650 nm, (see Fig. 4), which is reasonable to assign as DHDA-13 II* and DHDA-12 II* proton-transfer tautomer emissions. At the current stage, it is not feasible to apply fluorescence upconversion measurement for a single crystal of DHDA. Alternatively, the time-resolved studies were performed using the TCSPC technique with a system response time of ~20 ps. The results shown in Fig. S8 reveal that the DHDA-13_II* emission monitored at 520 nm consists of a fast relaxation decay (< system response time of 20 ps) and a longer decay component of 134 ± 5 ps. When monitored at 700 nm, assigned to the DHDA-12 II* emission, the time trace apparently consists of a system irresolvable rise component and a long decay component of 139 \pm 5 ps. Within experimental errors, the population decay times of DHDA-13_II* and DHDA-12_II* are identical, supporting the fast equilibrium relationship concluded in solution. The results reaffirm the dominant DHDA-23_OI conformer in the crystal form, in which ultrafast first proton transfer takes place, forming DHDA-13_II*, which then undergoes second proton transfer to yield DHDA-12_II*. DHDA-13_II* and DHDA-12_II* are in fast thermal equilibrium, giving rise to 520 and 650 nm emission bands with identical population decay time.



Figure 4. The comparative emission spectra of DHDA in cyclohexane (black) and in solid (red) at room temperature. λ_{ex} = 380 nm

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2.4 Theoretical Investigation We then present the computational approach in an aim to confirm the experimental observations. The calculated relative energies for various isomers in cyclohexane on the ground state (S_0) and the first excited state (S_1) are listed in Fig. 5. As shown in the Figure, on the ground state the DHDA-23_OO is found to be the lowest-energy isomer with DHDA-23_OI and DHDA-13 II about 0.9 and 2.2 kcal/mol, respectively, being higher in energies. The isomer **DHDA-12 II** is predicted to be not an energy minimum. The absorptions of DHDA-23_OO and DHDA-23_ OI are predicted at 383 and 396 nm, respectively. This is consistent with the experimental observation mentioned in previous sections. On the first excited state S₁, the DHDA-23_OI* is predicted to be not an energy minimum whereas the DHDA-12_II* is predicted to be a minimum-energy structure. As shown in Fig. 5, excitation from DHDA-23 OI would immediately cause an excited-state proton transfer and form the DHDA-13_II* isomer. A small intramolecular proton transfer barrier (~1 kcal/mol) separates DHDA-13_II* and DHDA-12_II* where the two excited-state isomers are almost isoenergetic. The small energy difference (-1.0 kcal/mol) is almost identical to the experimentally derived value (-0.9 kcal/mol). The calculated tautomer emissions from DHDA-13_II* and DHDA-12_II* are 491 and 610 nm, respectively, which are also in reasonable agreement with the experiment. It is also apparent that excitation from DHDA-23 OO would not lead to intramolecular proton transfer within the lifetime of the excited state due to the high barriers at TS2* and TS3* (see Fig. 5). Note that both TS3 (or TS3*) takes two steps from DHDA-23 OO (or DHDA-23 OO*) to DHDA-23_OI (or DHDA-23_OI*), incorporating the C(1)-O(3)-H(3) (see Fig. 1) rotation on the right phenyl ring and aldehyde rotation step (C(2)-C(12-O(4), see Fig. 1). The normal emission of DHDA-23 OO is predicted at 403 nm in cyclohexane, which is in good agreement with experimental results shown in Fig. 2 and Scheme 3. Finally, in CH₃CN DHDA-23 OO was calculated to be more stable by 1.3 kcal/mol than DHDA-23_OI, which is 0.4 kcal/mol more stable than that in cyclohexane. The result, in a qualitative manner, rationalizes the dominant normal emission upon increasing the solvent polarity. Also, according to the calculation, the normal emission red shifts from 403 nm to 426 nm in CH₃CN, which is consistent with the experiments (~30 nm in red shift, see Fig. S4)).



Figure 5. The calculated relative energetics for possible isomers of **DHDA** in the ground and first electronically excited states. One additional step between TS3 and DHDA-23_OI has been omitted for clarity.

3. Conclusion

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In summary, combining the spectroscopy/dynamics and computational approaches we have clearly shown that molecule DHDA containing at least two conformers in the ground state, in which DHDA-23_OI isomer undergoes a stepwise double protontransfer, giving the first and second proton transfer tautomers DHDA-13_II* and DHDA-12_II* that are in equilibrium. The other H-bonded isomer is ascribed to DHDA-23_00, for which both single and double proton transfer are energetically forbidden. As a result multiple emission bands are observed, consisting of normal DHDA-23 OO* emission (450 nm), first proton-transfer DHDA-13 II* emission (500 nm) and second proton-transfer DHDA-12 II* emission (650 nm) in cyclohexane. The computational approach calculation also predicts very minor ground-state population for DHDA-13_II* (< 5%). Unfortunately, we cannot confirm this prediction by either steady-state or dynamic approaches at current stage because the associated ESIPT dynamics, in theory, is the same as DHDA-23_OI that undergoes ultrafast (< 150 fs) first proton transfer. Due to the molecular packing, only DHDA-23_OI isomer exists in the crystal form, rendering a white light-like emission originating from first and second proton transfer tautomers that are in equilibrium in the excited state.

ASSOCIATED CONTENT

Supporting Information. Additional crystallographic (including CIF) and spectroscopic data are provided. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interests.

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The proposed double proton transfer model for DHDA