Multi-dimensional Hydrogen Bonds Regulated Emissions of Single Molecule Enabling Hydrophobicity/Hydrophilicity Mapping

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Abstract

Constructing multi-dimensional hydrogen bond (H-bond) regulated single-molecule systems with multi-emission remains a challenge. Herein, we report an excited-excited intramolecular transfer (ESIPT) featured chromophore (HBT-DPI) that shows flexible emission tunability via the multi-dimensional regulation of intra- and intermolecular H-bonds. The feature of switchable intramolecular H-bonds is induced via incorporating two hydrogen bond acceptors into a single-molecule system, HBT-DPI, allowing the "turn on/off" of ESIPT process by forming isomers with distinct intramolecular H-bonds. In response to different solvent environments, the obtained four types of crystal/cocrystals vary in the contents of isomers and the molecular packing modes, which are mainly guided by the intermolecular H-bonds, exhibiting non-emissive features or emissions ranging from green to orange. Moreover, we demonstrate the practical utility of this fluorescent material for visualizing hydrophobic/hydrophilic areas on large-scale heterogeneous surfaces of modified PVDF membranes and quantitatively estimate the surface hydrophobicity, providing a new approach for hydrophobicity/hydrophilicity monitoring and measurement.

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Abstract

Constructing multi-dimensional hydrogen bond (H-bond) regulated single-molecule systems with multiemission remains a challenge. Herein, we report an excited-excited intramolecular transfer (ESIPT) featured chromophore (**HBT-DPI**) that shows flexible emission tunability via the multi-dimensional regulation of intra- and intermolecular H-bonds. The feature of switchable intramolecular H-bonds is induced via incorporating two hydrogen bond acceptors into a single-molecule system, **HBT-DPI**, allowing the "turn on/off" of ESIPT process by forming isomers with distinct intramolecular H-bonds. In response to different solvent environments, the obtained four types of crystal/cocrystals vary in the contents of isomers and the molecular packing modes, which are mainly guided by the intermolecular H-bonds, exhibiting non-emissive features or emissions ranging from green to orange. Moreover, we demonstrate the practical utility of this fluorescent material for visualizing hydrophobic/hydrophilic areas on large-scale heterogeneous surfaces of modified PVDF membranes and quantitatively estimate the surface hydrophobicity, providing a new approach for hydrophobicity/hydrophilicity monitoring and measurement.

Introduction

Hydrogen bonding, as one of the most ubiquitous molecular interactions, plays important roles in modulating the properties and functions of advanced materials for numerous applications. ¹⁻⁸Especially, in the field of luminescent materials, the modulation of hydrogen bonds (H-bond) is linked with performances in the aspects of photoswitching,^{9,10} emission wavelength,^{11,12} luminescence lifetime,^{13,14} and quantum yield.^{15,16} Since the energy of ordinary H-bonds is normally less than 15 kcal/mol,¹⁷ environmental stimuli such as the temperature,¹⁸humidity,¹⁹ vapor,^{20,21} force,^{22,23} and solvents^{24,25} can interfere with the established H-bonds of the chromophores, making their emissions environment-sensitive.



Scheme 1. Design of model molecule HBT-DPI with multi-dimensional H-bonds.

Excited-state intramolecular proton transfer (ESIPT) is known as an H-bond dependent photophysical process that requires an intramolecular H-bond to trigger the enol to keto conversion upon photoexcitation, leading to a relatively large emission shift and high quantum yield.²⁶⁻²⁹ The strategy of shutting intramolecular H-bond via isomerization has been utilized to design smart ESIPT materials for anticounterfeiting,³⁰sensing,^{31,32} and force-response luminescent material.³³ Notably, a recently reported (2-(((1H-benzo[d]imidazol-2-yl)imino)methyl)-4-methoxyphenol system, which contains multiple H-bond donor and acceptors, exhibited a remarkable sensitivity in distinguishing heavy water from the water via the regulation of intermolecular H-bonds.³⁴ Despite the successes in their specific applications, these ESIPT chromophores possess limited emission alterations due to insufficient diversity in the regulation of intra-and intermolecular H-bonds. It is worth noting that intermolecular H-bond governed molecular packing reconstruction is a major strategy to accomplish emission alterations in many fluorescent materials^{35,36} other than ESIPT fluorophores, which suggests a potential but challenging route to extend the tunability in photochemical properties and application scenarios of ESIPT systems via regulating intra- and intermolecular H-bonds.

Surfaces are fundamental and prevalent in nature and industry, whose surface properties, especially hydrophobicity/hydrophilicity, are of great importance in many practical applications, such as biological adhesion,^{37,38} coating, ^{39,40} anti-fogging, ⁴¹ oil-water separation,^{42,43}, and catalysis. ⁴⁴Thereby, characterizations of surface hydrophobicity/hydrophilicity are critical in understanding and controlling the surface behaviors. However, the conventional contact angle method falls short in offering a comprehensive measurement on such surfaces, while the heterogeneity might also lead to uncertainties in measurements. ⁴⁵Considering that the abundance of interfacial H-bond acceptors is closely relevant to the surficial hydrophobicity/hydrophilicity,⁴⁶⁻⁴⁸ fluorescence-based method that is sensitive to H-bonding might offer a solution to complement the contact angle method in the scenario of large-scale heterogeneous surfaces. In this study, we explored the potential of multi-dimensional regulation of intra- and intermolecular H-bonds in single molecule ESIPT systems to expand the variety of emissions. We designed and synthesized a model ESIPT chromophore **HBT-DPI** by incorporating a diphenylimidazole (**DPI**) group into **HBT** (Scheme 1). Unlike conventional ESIPT chromophores, the presence of two H-bond accepting groups (HBAs), benzothiazole (**BT**) (HBA-1) and **DPI** (HBA-2), provides an extra choice for the intramolecular H-bond with the hydroxyl group in the phenol core. Moreover, the N-H in imidazole, as an H-bond donor, along with the bulky diphenyl group could offer flexibility in subtle modulation of intermolecular H-bond formation. In response to different solvent environments, four types of **HBT-DPI** crystal/cocrystals showed diversity in the contents of structural isomers, molecular packing modes, and photophysical properties, resulting from the varied behaviors in intra- and intermolecular H-bonds formation. Notably, we successfully employed **HBT-DPI** to visualize the surficial hydrophobicity/hydrophilicity distribution along with their quantification on heterogeneously modified PVDF membranes, demonstrating a new approach for hydrophobicity/hydrophilicity monitoring and measurement on a large-scale surface with heterogeneous modification. Overall, this study provides a new strategy to construct ESIPT-inspired chromophores whose single molecular emissions are regulated by multiple-dimensional H-bonds, and demonstrated the unique application in hydrophobicity/hydrophilicity mapping on a large-scale heterogeneous surface.

Results and Discussion

Molecular design and synthesis.

To enable the multi-dimensional regulation of H-bonds, **DPI** was attached to a central **HBT** core to obtain the model ESIPT chromophore **HBT-DPI**. Although both **DPI** and **BT**contain unsaturated N atoms, endowing them with excellent H-bond accepting capability, whereas the presence of sulfur atom in **BT**weakens its hydrogen accepting ability.^{49,50} Moreover, the **DPI** group contains an extra H-bond donor (N-H) that can form either an intramolecular H-bond with the oxygen of the phenol core or an intermolecular H-bond with other molecules, which could extend the possible molecular packing behaviors in the solid state. By such a molecular design, the manipulation of multi-dimensional H-bonds (intra- and intermolecular) would render the environment sensitive material with a variety of photophysical properties. The ESIPT chromophore**HBT-DPI** was synthesized by three-step reactions according to Supplementary Scheme S1 and characterized using ¹H NMR, ¹³C NMR and high-resolution mass spectrometry (Figures S20-22).

Solvent-induced isomerization and photophysical properties of HBT-DPI.

We first investigated the intramolecular H-bond switching in solution. Although HBT-DPI exhibits similar absorption bands (280-400 nm) in the tested solvents (Figure S1), the fluorescent emission spectra of HBT-DPI were found to be much stronger in the solvents containing O or N atoms that can act as H-bond acceptor (including ethyl acetate (EtOAc), tetrahydrofuran (THF), dioxane (DIO), acetone (ACE), alcohol (EtOH), methanol (MeOH), acetonitrile (ACN), N, N-dimethylformamide (DMF), dimethyl sulfoxide (DMSO)) than in those without H-bond acceptor (including n -hexane (n -Hex), toluene (TOL), dichloromethane (DCM) and chloroform (TCM)) (Figures 1A and 1B), implying different molecular status in the two types of environments. Quantum chemical calculations reveal that, in TCM (without an H-bond acceptor), HBT-**DPI** tends to form the isomer**OH-BS** which is stabilized by two intramolecular H-bonds to achieve the lowest potential energy (Figure 1C). In contrast, the O atom in THF competes for the free hydrogen of **DPI**. forming a strong N-H...O intermolecular H-bond (Figure S2); while the imidazole, a stronger H-bond acceptor than **BT**, preferentially forms the intramolecular H-bond with the hydroxyl in phenol core, representing the isomer **OH-DPI** (Figure 1C). After demonstrating the two isomers with switched intramolecular H-bonds. further analysis shows that the keto form of **OH-DPI** has a significantly larger oscillator strength (f) of 0.8695 than the end form of **OH-DPI** and the vertical keto*-keto photoluminescence peak is calculated to be 513 nm for **OH-DPI** (Figure 1D), which is consistent with the experimental data, indicating the emissive ESIPT process of **OH-DPI** isomer. Whereas **OH-BS** possesses a weak emission mainly due to the fast nonradiative decay process caused by the large reorganization energy of 0.964 eV (Figure 1E). Besides, we also found that the energy barrier of possible transforming routes between **OH-DPI** and **OH-BS** is relatively small in TCM (Figure S3). The small energy barrier would allow a partial transition from **OH-BS** to **OH-**

DPI, contributing to the retention of fluorescence emission in TCM and possibly other solvents without H-bond acceptor. Additionally, when increasing the content of THF in the n -Hex solution, the fluorescence intensity of **HBT-DPI**significantly increased (Figure S4), indicating the occurrence of isomerization from **OH-BS** to **OH-DPI**. These results demonstrate the success of our molecular design on intramolecular H-bond switching, which can be controlled via the hydrogen accepting capability of solvent.



Figure 1. Solvent-induced isomerization and theoretical calculation. (A) Fluorescence spectra (10 μ M) of HBT-DPI in different solvents, green lines: with strong emission, blue lines: with weak emission, *n* -Hex: *n* -hexane, TOL: toluene, DCM: dichloromethane, TCM: chloroform, EtOAc: ethyl acetate, THF: tetrahydrofuran, DIO: dioxane, ACE: acetone, EtOH: alcohol, MeOH: methanol, ACN: acetonitrile, DMF: N, N -dimethylformamide, DMSO: dimethyl sulfoxide, $\lambda_{ex} = 365$ nm, slit: 5 nm/5 nm. (B) Statistics of fluorescence and wavelength changes in various solvents. (C) Chemical structure and the energy of OH-BS andOH-DPI in different solvents. (D) The schematic representation of the ESIPT state of OH-DPI in THF solvents. (E) Potential energy surfaces of OH-BS in TCM solvents. The relative energies (in eV) and oscillator strengths (f) were evaluated at the level of (TD)DFT/O3LYP/def2-SVP.

Multimodal H-Bonds induced multiple optical behaviors in crystals.

To further demonstrate the multi-dimensional regulation of intra- and intermolecular H-bonds in **HBT-DPI** and the resulting diverse photochemical properties, we prepared single crystals of **HBT-DPI** in various solvents. As expected, we successfully obtained four types of **HBT-DPI** single crystals (**HBT-DPI-N**, **HBT-DPI-Y**, **HBT-DPI-G**, and **HBT-DPI-O**) with distinct photophysical behaviors by the solvent-induced method. Through the single-crystal X-ray diffraction (SXRD) analysis, we found that the crystals

exhibit varieties in the contents of **HBT-DPI** isomers and the molecular packing behaviors (Figure 2. Figures S5-8 and Tables S9-10), which are largely influenced by the strong H-bonds (distance between hydrogen atom and H-bond acceptor < 2.2 Å, bond energy around -4 to -15 kcal/mol).¹⁷ The single crystal of HBT-DPI-N was first obtained from a gas (n - pentane)-liquid (TCM) diffusion system. Due to the absence of competitive intermolecular H-bonds between imidazole moiety and solvent molecules, two types of strong intramolecular H-bonds including O1-H. N1 (1.859 Å) and N3-H. O1 (2.119 Å) were constructed in**HBT-DPI-N** corresponding to **OH-BS** isomer (Figure 2C). The specific double intramolecular H-bonds system endows considerable reorganization energy, suppressing the emission of the **OH-BS** isomer (Figures 2B and 2F). Moreover, the severe π - π stacking (r1 = 3.541 Å) of crossing packing mode further consumes the excited state energies (Figure S5), thus quenching the fluorescence emission in the crystalline state (Φ $_{\rm F}$ < 0.001) (Figures 2J-K). While an enhanced fluorescence quantum yield ($\Phi_{\rm F} = 10.54\%$) can be obtained in **HBT-DPI-Y** cocrystals prepared by evaporating n -Hex and DCM mixture (Figures 2C and 2J-K). The **HBT-DPI-Y** cocrystals formed a new intramolecular H-bond (N2...H-O1, 1.793 Å), which corresponds to the **OH-DPI** isomer (Figure 2G), facilitating the activation of ESIPT process. Unlike TCM, DCM molecules were trapped in the **HBT- DPI-Y** cocrystals, providing multiple interactions containing halogen bond (Cl… # 4.007 Å), H-bond (C-H…N2 2.637 Å, C-H…Cl 2.852 Å, C-H…Cl 2.915 Å) and C-H… # (2.807 Å) (Figure S6A), along with the intermolecular H-bonds (N3-H…N1, 2.192 Å) among**OH-DPI** isomers, triggering the formation of an interlock crossing packing mode, which contributes a vellow fluorescence emission at 549 nm (Figures 2C and S6).

In response to THF that offers H-bond acceptors, a type of green fluorescence cocrystals **HBT-DPI-G** ($\lambda_{\rm em} = 505$ nm) was collected (Figure 2D). The THF molecule formed an intermolecular H-bond with **HBT-DPI** between N3-H and the oxygen atom (O2) of THF (Figure 2H), benefiting the formation of the **OH-DPI** isomer. The antiparallel packing mode found in the cocrystals **HBT-DPI-G**enlarges the centroid distance of adjacent molecules to avoid the π - π stacking (Figures S7B-C), rendering the promoted $\Phi_{\rm F}$ of 26.07% (Figures 2J-K). Intriguingly, a triad cocrystal species **HBT-DPI-O** was obtained from the protic EtOH. As shown in Figure 2I, both the **OH-BS** and **OH-DPI** isomers were found in **HBT-DPI-O** at a 1:1 molar ratio. Possessing both the H-bond donor and acceptor, EtOH tethers a pair of **OH-BS** and **OH-DPI** via two intermolecular H-bonds (N3-H…O3 2.168 Å, O3-H…N2 1.994 Å) (Figure 2I); and the paired units pack organized, leading to red-shifted fluorescence emission at 564 nm with a reduced $\Phi_{\rm F}$ (6.02 %) (Figures 2E and 2J-K), which could be due to the existence of **OH-BS** isomers, π - π stacking and other concomitantly abundant intermolecular interactions (Figure S8). The discovery and characterizations of the four crystals demonstrated the success of tuning the photophysical behaviors of **HBT-DPI** via multi-dimensional regulation of intra- and intermolecular H-bonds.

Further attempts revealed that **HBT-DPI-N** can also grow in the solvent without H-bond acceptor, such as TOL (Figures S9 and S11A, Table S11); in contrast, the solvents with H-bond acceptor, including ACN, DIO, and ACE, favor the formation of **HBT-DPI-G** (Figures S10 and S11B-D, Tables S11-12). The orange emission similar to**HBT-DPI-O** was also observed in powders obtained from MeOH, which was confirmed to have a similar structure with **HBT-DPI-O**by X-ray diffraction (XRD) (Figures S12 and S13), suggesting the packing mode of **HBT-DPI-O** might be favorable in alcohols. Whereas the distinct packing mode of **HBT-DPI-Y** was only found in the crystal prepared in DCM. Overall, these results prove that the multi-dimensional regulation of intra-/intermolecular H-bonds offers extra diversity in constructing multi-emissive environment sensitive materials.





Figure 2. Multimodal H-Bonds induced multiple optical behaviors in crystals. (A) Isomerization of **HBT-DPI** between**OH-BS** (black) and **OH-DPI** (purple). Fluorescence spectra of the crystal obtained in (B) TCM (**HBT-DPI-N**), (C) DCM (**HBT-DPI-Y**), (D) THF (**HBT-DPI-G**), (E) EtOH (**HBT-DPI-O**), $\lambda_{ex} = 365$ nm, slit: 5 nm/5 nm, inset: crystal pictures (top right-hand corner) and fluorescence photographs (bottom right-hand corner), TCM: chloroform, DCM: dichloromethane, THF: tetrahydrofuran, EtOH: alcohol. Crystal structures and intra-/intermolecular H-bonds of (F) **HBT-DPI-N**, (G)**HBT-DPI-Y**, (H) **HBT-DPI-G**, (I) **HBT-DPI-O**composed by **OH-BS** (black) and **OH-DPI** (purple). (J) Table of the wavelength, molecular states, H-bonds and absolute fluorescence quantum yields of crystals. (K) The fluorescence spectra of **HBT-DPI-G**, **HBT-DPI-G**, **HBT-DPI-F**, and **HBT-DPI-O** tagged on a CIE 1931 chromaticity diagram.

Monitoring hydrophilic and hydrophobic properties on membrane surface.

Inspired by the H-bond acceptor sensitive nature of **HBT-DPI**, we tried to sense the surficial hydrophilicity and hydrophobicity using **HBT-DPI**. **HBT-DPI** emitted green emission upon polycarbonate (PA) membrane (hydrophilic surface) and yellow emission upon hydrophilic membranes containing poly(1,1difluoroethylene) (PVDF), polypropylene (PP) and polytetrafluoroethylene (PTFE), demonstrating the outstanding property of our fluorophore (Figures S14 and 3A). On this basis, we tried our fluorophore to monitor the modified membranes, which showed extensive requirement and application in material science.^{39,51,52} We used PVDF membrane as the model surface and created hydrophilic areas using Sub-Atmospheric Microthermal Plasma (SAMP). The original PVDF membrane surface was hydrophobic with a contact angle of around 128.3° (Figure 3A), and the subsequent treatment of SAMP increased the surface hydrophilicity, rendering a contact angle of around 26.7° (Figure 3B). The oxygen contents intensified by the SAMP treatment at the membrane surface (Tables S1 and S2) increase the hydrophilicity while also acting as the H-bond acceptors. Consequently, by sensing the H-bond acceptors, the green coating of **HBT-DPI** on the original PVDF membrane surface (Figure 4A) turned to yellow on the modified surface (Figure 3B), demonstrating the potential of **HBT-DPI** on distinguishing between hydrophilic and hydrophobic areas.



Figure 3. Monitoring hydrophilic/hydrophobic surface. The fluorescence spectra of membrane (A) before and (B) after modification of PVDF membrane staining by **HBT-DPI**, inset: diagram of contact angle measurement (left) and colored membrane (right). (C) Stabilized packing mode of **HBT-DPI** adsorption on the original PVDF, blue background: solvents (DCM). (D) Stabilized packing mode of **HBT-DPI** adsorption on the modified PVDF, blue background: solvents (DCM). (E) Topological parameters of the interaction between PVDF (green background) or modified PVDF (yellow background) and **HBT-DPI**. (F) **HBT-DPI** adsorbed on the modified PVDF surface and the parameter of the N-H…O H-bond. Color code: white, H; sky blue, C; yellow, S; blue, N; red, O; Orange, F.

Further theoretical calculations explored the molecular behaviors of **HBT-DPI** on the model surfaces to explain the changed fluorescent emissions (details of theoretical calculations are available in section 14 of the supplemental information). Since the original PVDF membrane lacks efficient HBAs, only weak H-bonds (C-H…F) formed between **HBT-DPI** molecules and the membrane (Figure 3E), leading to parallelly piled **HBT-DPI** molecules which emit green fluorescence on the membrane surface (Figures 3C and S15A-D, Video S1). In contrast, the abundant oxygen (Tables S1 and S2) on the modified PVDF surface leads to the formation of abundant H-bonds (C-H…F, C-H…O and N-H…O) with **HBT-DPI** molecules, resulting in much stronger affinity between the modified surface and **HBT-DPI** (Figures 3E, S16 and S17). Especially, the bond energy and length of the N-H…O bond is calculated as -4.27kcal/mol and 2.06 Å (Figures 3F and S18, Table S3), providing dominant interactions to trigger the cross-stacking mode of molecular assembly (Figures 3D and S15E-H, Video S2), which corresponds to a yellow fluorescence according to the aforementioned SXRD analysis (Figure 2E).

Quantitative evaluation of surface hydrophobicity/hydrophilicity.

Considering the relevance between the abundance of oxygens and hydrophilicity, the intensity ratio between

the external H-bond-induced yellow emission ($\lambda_{em} = 549 \text{ nm}$) and the green emission ($\lambda_{em} = 505 \text{ nm}$) of **HBT-DPI** should be able to quantitatively evaluate the surficial hydrophobicity. As a proof of concept, several PVDF membranes with varying surficial hydrophobicity were prepared via plasma modification from 0 to 180 s. The contact angle (ϑ) for each modified PVDF membrane surface was measured within the range of 20-130° (Figure S19 and Table S4). Afterward, the membranes were coated with **HBT-DPI** as mentioned above to collect the ratios of I_{549}/I_{505} (Figure 4A). By plotting I_{549}/I_{505} versus $\cos\vartheta$, the calibration curve between the I_{549}/I_{505} and its corresponding ϑ was defined by a linear equation, $I_{549}/I_{505} = 3.10\cos\vartheta + 2.83$ (Figures 4C and S19, Tables S4 and S6). Owing to the influence of non-uniform surface textures, the measurement of the fluorescence intensity showed variations, resulting in an \mathbb{R}^2 of 0.9787 for the calibration curve. Despite the slightly low \mathbb{R}^2 , we can still conclude the linear relationship between I_{549}/I_{505} and $\cos\vartheta$, and the **HBT-DPI** fluorescence intensity ratio of I_{549}/I_{505} increases along with the increasing $\cos\vartheta$, which represents enhanced hydrophilicity.

On this basis, we further prepared a PVDF membrane with a partially modified surface by covering a porous mask before plasma treatment (Figures 4A and 4B). The purpose is to create unevenly distributed hydrophilic areas on the membrane surface. As expected, after merging the membrane in DCM solution containing **HBT-DPI** and drying, yellower patterns consistent with the pores on the mask were seen while the covered area, which is less irradiated, maintained green color (Figures 4B and 4D). The observation convincingly demonstrates the unique merits of **HBT-DPI** in mapping the distribution of hydrophilic and hydrophobic areas on a large-scale surface, which is not feasible with the conventional contact angle method. We also estimated a mean hydrophobicity of the heterogeneous surface by corresponding the I_{549}/I_{505} ratio to a calculated contact angle (Figures 4C and Table S8). For instance, the modified membrane 1 exhibited an I $_{549}/I_{505}$ ratio of 1.29 corresponding to a ϑ of 126.2°, while the modified membrane 2 with more hydrophilic areas gave an I_{549}/I_{505} ratio of 2.28 corresponding to a ϑ of 104.6° (Figures 4C and 4D, Table S8). Although the calculated contact angle via **HBT-DPI** mapping is not representing a specific hydrophobicity of any point on the surface, it can provide information on the overall hydrophobicity of a heterogenous and large-scale surface, which is not able to be estimated before. Taken together, our examples demonstrate the potential of **HBT-DPI** as a convenient and useful tool to evaluate the surficial hydrophobicity/hydrophilicity, and its advantages over the conventional method in the aspects of mapping the hydrophobic/hydrophilic areas as well as quantification on a large-scale surface, even the surficial modification is heterogeneous.



Figure 4. Quantitative evaluation of surficial hydrophobicity/hydrophilicity. (A) Process of surficial modification, top: the process of obtaining complex surface, bottom: the process of obtaining standard curve. Concentration of **HBT-DPI** in DCM solution: 1mM. (B) Complex surface modified by coving a mask, left: the mask, right: complex surface after stained by **HBT-DPI**. (C) The standard curve between fluorescent ratio and contact angle upon the PVDF membrane. (D) The comparison of hydrophobicity between various large-scale surfaces.

Conclusion

In summary, we proposed to extend the diversity in constructing single-molecule ESIPT systems by the multidimensional regulation of intra- and intermolecular H-bonds. The model molecule, HBT-DPI, reported in this work contains two functional groups, diphenylimidazole (**DPI**) and benzothiazole (**BT**), which render the feature of switchable intramolecular H-bonds. Two isomers, OH-DPI and OH-BS, were obtained respectively in solvents with or without H-bond acceptors, possessing distinct intramolecular H-bonds that influence the ESIPT process to the emissive properties of the two isomers. In response to different solvent environments, four types of HBT-DPI crystal/cocrystals (HBT-DPI-N, HBT-DPI-Y, HBT-DPI-G and **HBT-DPI-O**) were further obtained via crystal growth as a result of the regulation of both intra- and intermolecular H-bonds. The multi-dimensional H-bonds regulation largely influenced the molecular packing of **HBT-DPI** molecules, resulting in multimode crystal structures that are non-emissive or emit variable fluorescence ranging from green to orange. This work provides new insights into the H-bonds regulation induced structure-packing-performance relationship, which offers a molecular-level design strategy to construct single molecule light-emitting materials with multi-emissions. Furthermore, HBT-DPI was shown to map the hydrophobic/hydrophilic areas on large-scale heterogeneous surfaces and quantitatively estimate the surficial hydrophobicity/hydrophilicity, offering a new approach advantageous over the conventional contact angle measurement.

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Author Contributions

Hao Gu: Methodology, Formal analysis, Writing – original draft, Validation, Data curation, Writing – review & editing. Rui Li: Writing – review & editing, molecular dynamics cal-culations. Qiuying Li: Writing – review & editing, quantum chemical calculation. Sheng Lu: Writing – review & editing, data curation. Yahui Chen: Data curation, Visualization. Xiaoning Yang: Visualization. Huili Ma: Writing – review & editing, Supervision, Funding acquisition. Xiaoqiang Chen: Writing – review & editing, Supervision, Funding acquisition. Xiaoqiang Chen: Writing – review & editing, Supervision, Funding acquisition.

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