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Review

Role of Hydrogen Transfer in Functional Molecular Materials and Devices

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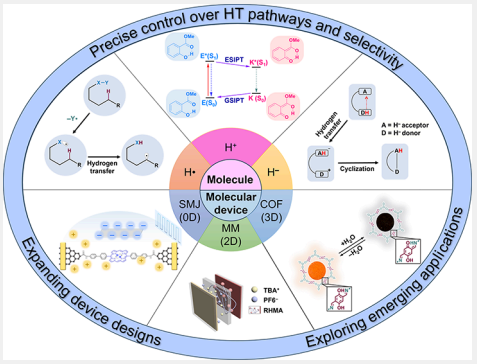
ABSTRACT: Hydrogen transfer is a fundamental chemical process critical to the design and application of organic molecules and functional devices. By uncovering the dynamic interactions between atoms within molecules, hydrogen transfer research offers innovative pathways for creating advanced functional materials and devices. These advancements have driven progress in areas such as optoelectronics, molecular switches, and bioimaging. This review explores the various forms of hydrogen transfer, including hydrogen atom, proton, and hydride transfer, highlighting their mechanisms and key reactions. It also examines the integration of these processes into molecular devices, including single-molecule systems, molecular films, and organic frameworks. Future directions emphasize precise control of hydrogen transfer pathways, development of highly selective and efficient reaction systems, and the design of robust devices based on these processes. These efforts aim to enhance device performance and broaden applications in intelligent materials, integrated functions, and information technology.



KEYWORDS: *Hydrogen transfer, Proton transfer, Hydride transfer, Molecular electronics, Single-molecule device, Organic frameworks, Molecular membrane*

1. INTRODUCTION

Hydrogen transfer (HT) is a fundamental chemical process prevalent in both natural and artificially designed molecular systems. It encompasses the migration of hydrogen atoms (H•), protons (H^+), and hydride ions (H^-) within and between molecules. The exploration of HT begins with understanding molecular reactivity and dynamics, particularly in classic Brønsted acid−base reactions,[1] enzymatic catalysis,[2] and photochemical processes.[3] HT not only affects atomic and electronic distributions but also determines molecular stability and reactivity, serving as catalysts or intermediates to regulate reaction rates, selectivity, and energy transfer efficiency. Extensive research has elucidated various HT mechanisms, including free radical-mediated hydrogen atom transfer[4] (HAT), excited-state intramolecular proton transfer[5] (ESIPT), and hydride transfer based on *tert*-amino effect,[6] etc. These processes span microscopic physical chemistry mechanisms, such as bond formation and cleavage, as well as macroscopic phenomena like intermolecular cooperation and external field regulation. For example, ESIPT is integral to optoelectronics,[7] biomedicine[8] and sensors.[9] As molecular science progresses, controlling HT reactions has become a crucial challenge and opportunity in reaction design.

Along with the rapid development of nanotechnology, molecular electronics, and optoelectronic science, HT research has expanded from probing reaction mechanisms[10−12] to serving as a strategy for designing novel functional materials and devices.[13−15]

Despite significant progress, substantial challenges remain in the practical applications of HT in functional molecules and molecular devices. The key challenges in extending HT processes to broader applications lie in achieving precise control over HT pathways and selectivity. This includes overcoming current reaction condition limitations, predicting and controlling pathways and mechanisms in complex molecular systems, and developing efficient and stable HT regulation in complex environments. Moreover, integrating HT processes with device performance demands further exploration. Future efforts should focus on developing highly selective and efficient HT systems, enhancing device stability and responsiveness, and exploring broader applications in intelligent materials, integrated systems, energy conversion, and information technologies. This review aims to provide a

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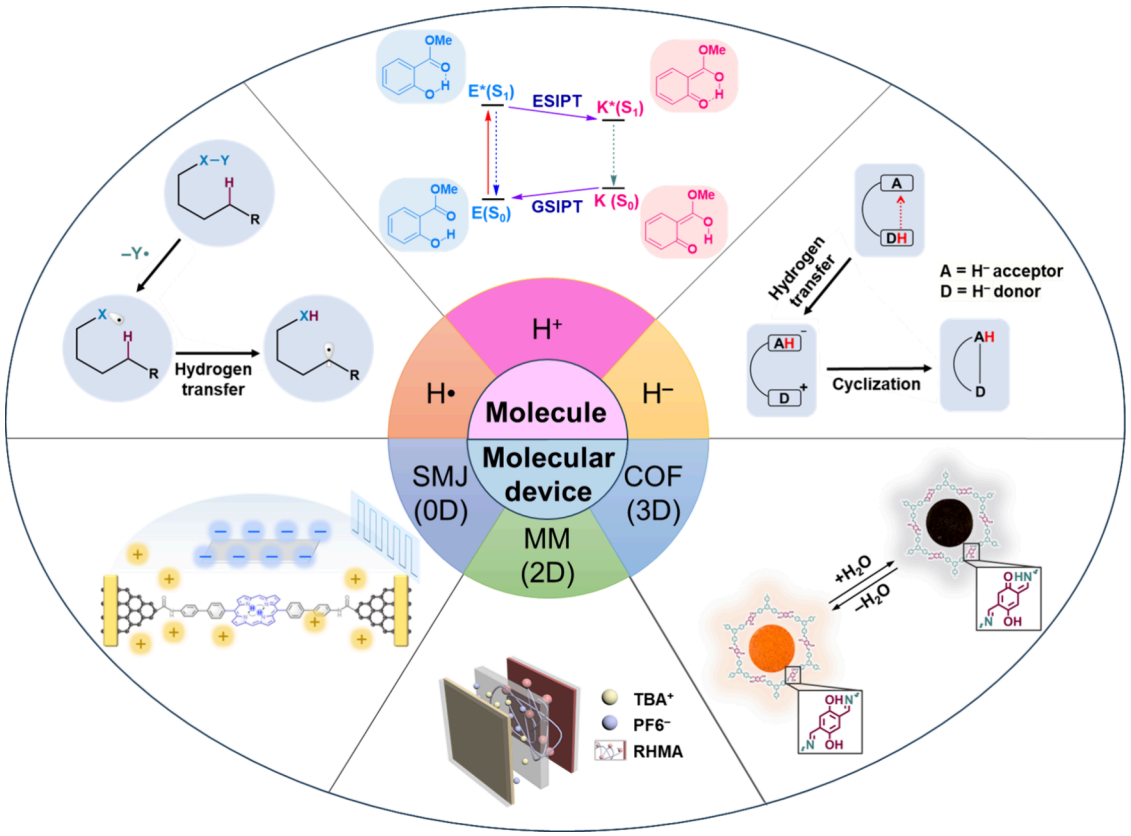

Figure 1. Overview of hydrogen transfer mechanisms and their applications in functional molecules and molecular devices. Intramolecular hydrogen transfer mechanisms (top): intramolecular hydrogen atom transfer (left), representative reaction mechanism of intramolecular proton transfer (middle), and intramolecular hydride anion transfer (right). Intramolecular hydrogen transfer devices (bottom): single-molecule junction (left), molecular membrane (middle), and covalent-organic framework (right).

comprehensive perspective on the mechanisms, applications, and potential of HT, with the goal of inspiring further breakthroughs from fundamental theories to practical applications in the field (Figure 1).

2. HYDROGEN TRANSFER IN MOLECULES

Hydrogen transfer is a crucial reaction process across diverse scientific domains, including chemistry, materials science, and biology. It involves the migration of hydrogen atoms, protons, and hydride ions within or between molecules. This process is primarily determined by thermodynamic stability and kinetic feasibility and is often accompanied by the reorganization of electronic structures and chemical bonds. HT can proceed via atomic tunneling or through intermediates and transition states. These mechanisms not only emphasize the importance of precisely understanding molecular transformations but also provide critical insights into building complex molecular architectures. For example, radical-mediated HAT reactions, stimulated by radical generation strategies, have considerably broadened the scope of selective functionalization of distal C–H bonds.[4] In contrast, nonradical-mediated HAT processes utilize mechanisms such as metal–hydrogen bond cleavage,[31] hydrogen-bond network formation,[32,33] and electron transfer coupling to achieve superior selectivity and efficiency under mild conditions.[34,35] Proton transfer, which is closely related to the electronic structure of molecules, holds great significance in catalysis and biological processes.[8,36] Hydride anion transfer opens up new pathways for rearrangement and heterocyclization reactions by promoting the formation of stable intermediates.[37−42] These studies on hydrogen transfer in molecules provide valuable insights and potential for advancing organic synthesis, catalytic reactions, bioenergy transfer, and the development of sensors and photofunctional materials.

2.1. Intramolecular Migration of Hydrogen Atoms

Intramolecular hydrogen atom transfer refers to the process in which a hydrogen atom transfers from one atom or group to another within the same molecule, constrained by covalent bonds. It is very common in organic synthesis, catalytic reactions, and biological processes. This migration can occur through various pathways, mainly classified into radical-mediated (involving bond cleavage and radical formation) and nonradical-mediated (not involving radical intermediates) HAT reactions. In this section, we present an overview of the fundamental principles and mechanisms of various HAT reactions, highlight key reactions, and discuss the current advancements in this field.

2.1.1. Radical-Mediated HAT Reactions. Radical-mediated intramolecular HAT typically involves the following four key steps[4] (as shown in Figure 2):

2.1.1.1. Generation of Radical Precursors. Radical precursors are produced through various methods, including irradiation, electrochemical processes, or thermal excitation, yielding species such as alkyl, amino, or hydroxyl radicals.

2.1.1.2. Formation of Active Radicals. The precursors undergo chemical reactions, such as photocatalysis or redox reactions, within the molecule, generating highly reactive radicals.

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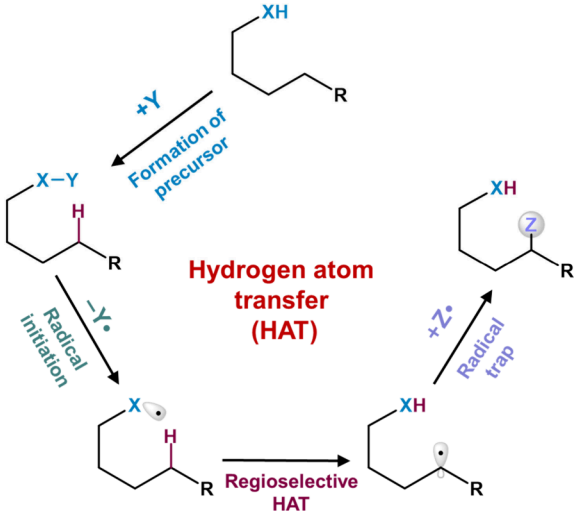

Figure 2. Schematic diagram of the key steps involved in radical-mediated HAT reactions, including formation of precursor, radical initiation, regioselective HAT and radical trap. Reproduced from ref 4. Copyright 2018 Thieme Group.

2.1.1.3. Regioselective HAT. The active radical extracts a hydrogen atom from a specific site within the molecule, initiating hydrogen migration. The regioselectivity of the transfer is influenced by bond energy differences, spatial configuration, and intramolecular interactions.

2.1.1.4. Radical Capture by an External Reagent. After hydrogen transfer, the resulting radical is stabilized by reacting with an external capturing agent, thereby forming a new chemical bond.

In promoting intramolecular hydrogen atom transfer, the first step is locking the radical precursor, typically achieved through a two-electron pathway to generate the key single-electron intermediate. Radical precursors can be classified into carbon-based (C), nitrogen-based (N), and oxygen-based (O) radicals,[43] which are commonly generated through dehydrogenation or oxidation reactions of alkyl halides and nitrogen compounds. Unlike the conventional conditions of the first step, the second step—the formation of the active radical—represents the most limiting aspect of HAT chemistry. Traditional strategies often employ harsh conditions, such as strong acids, high temperatures, unstable peroxides, toxic organotin reagents, or ultraviolet light. However, in recent years, with persistent efforts by scientists, milder methods have been developed for generating radicals. These methods use abundant metals such as iron, copper, and nickel, hypervalent iodine reagents, and visible light-mediated photocatalysts, making it possible to obtain radicals under milder conditions. In the third step, hydrogen atom transfer, the 1,5-HAT pathway is the most common for two main reasons. From a

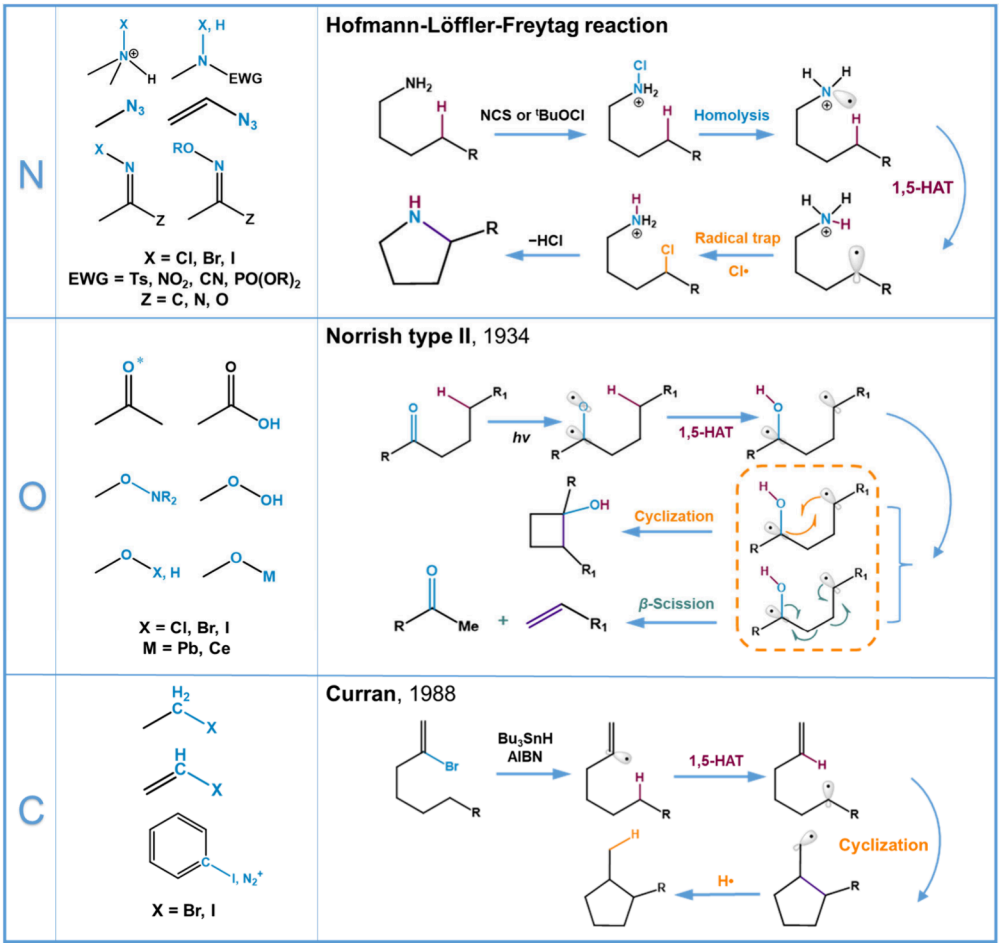

Figure 3. Illustration of three common radical precursors classified according to elements N, O and C, and the most classical HAT mechanism in each category. Reproduced from ref 4. Copyright 2018 Thieme Group.

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thermodynamic perspective, the bond dissociation energies of N−H and O−H bonds are higher than those of C(sp^3)−H bonds (approximately 105 kcal·mol^{-1} and 90−100 kcal·mol^{-1}, respectively), indicating that the 1,5-HAT process is thermodynamically favorable. From a kinetic perspective, although radicals are electrically neutral, the transition state in the 1,5-HAT process carries partial charge. Therefore, when an electrophilic radical species extracts a hydrogen atom from an electron-rich C−H bond, it has a lower activation energy compared to removing hydrogen from a similarly strong but electron-poor bond. Finally, the completion of HAT depends on the capturing agent used. Radical traps can range from cage-like radicals (X•, NO•, ON•), weakly bonded main group molecules (N−X, Si−X, Sn−H, Sn−allyl), metal salts (CuX, CuSCN, CuN_3), to π systems (alkenes, aromatics). This diversity in termination mechanisms allows C−H functionalization to achieve the broadest range of reactivity through any single pathway. Next, we provide a detailed discussion of important reactions and recent research advances in HAT, based on radical precursors (Figure 2).

2.1.1.5. N Radical. In the field of intramolecular HAT chemistry, nitrogen-centered radicals play a pivotal role. The polarity of these radicals can be finely tuned through N-substituents, making them some of the most versatile radicals, as their polarity has a significant impact on the reactivity of HAT processes. In 1883, Hofmann reported the earliest example of selective C−H functionalization via HAT.[44] This N-centered radical reaction is now known as the Hofmann-Löffler-Freytag (HLF) reaction (mechanism shown in Figure 3), which originates from the homolytic cleavage of a cationic *N*-halamine under photolysis. The resulting aminyl cation radical, which has sufficiently high polarity, can extract a hydrogen atom from a δ-carbon, generating a new C-centered radical. The regioselectivity of this 1,5-HAT process is controlled by a transition state resembling a chair conformation. The δ-carbon radical is then captured by recombination with a cage-like X• (or N−X), forming a δ-halo compound, which is subsequently replaced through base-induced intramolecular cyclization. This strategy, where amines undergo δ-C−H amination to synthesize pyrrolidine derivatives, simplifies the synthesis of various natural products and their derivatives. Currently, azides are used as replacements for halohamines, serving as precursors to N-centered radicals and achieving similar reactivity.[45] Additionally, imino N(sp^2)-centered radicals exhibit complementary reactivity compared to amino N(sp^3)-centered radicals.[46] Iminyl radicals react more rapidly with alkenes and undergo slower intermolecular hydrogen atom reduction reactions compared to neutral amino radicals. This unique kinetic behavior of N(sp^2)-centered radicals opens up distinct synthetic pathways. Thanks to the tireless efforts of researchers, N-centered radicals can now be generated through a wide range of mild radical initiation methods, such as metal porphyrin catalysts[47] and I_2.[48,49]

2.1.1.6. O Radical. Another common initiator of intramolecular HAT is the oxygen-centered radical. The more electronegative oxygen atom (χ = 3.4 for O vs 3.0 for N or 2.5 for C) provides a stronger driving force for HAT, due to two related factors: (1) the high electronegativity of oxygen, which makes its bond dissociation more difficult—second only to fluorine, thus promoting HAT; and (2) the O−H bond formed during HAT is relatively strong (BDE = 110 kcal·mol^{-1} for O−H vs N−H and C−H, both <100 kcal·mol^{-1}). Due to these inherent advantages, oxygen-centered radicals have become one of the most versatile synthetic radicals, capable of capturing intermediate carbon radicals by halogens, heteroatoms, or even alkyl groups. The most critical step in this mechanism is the generation of a radical on the electronegative oxygen atom, typically through three common pathways: carbonyl photoexcitation, alkoxy, and nonalkoxy initiation. The earliest example of oxygen-centered radical-mediated HAT was reported by Norrish, who demonstrated that photoexcitation of alkyl or aryl ketones containing a γ-C−H bond generates a 1,4-biradical (reaction mechanism shown in Figure 3).[50] Upon excitation of the ketone, the highly reactive oxygen radical undergoes 1,5-HAT, generating a 1,4-biradical intermediate that retains two carbon-centered radicals. Depending on the nature of the excited state, the biradical species either recombines to form cyclobutanols (via the triplet state, T_1) or undergoes β-cleavage to yield enols and alkenes (via the singlet state, S_1). In addition to carbonyl photoexcitation, oxygen-centered radicals can also be initiated through alkoxy and nonalkoxy methods. For alkoxy-based initiation, a recent approach has developed an alternative that excludes organotin, where light-activated Ir catalysts serve as single-electron transfer (SET) reducing agents to reduce the N−O bond, generating phthalimide anion and alkoxy radicals.[51,52] Non-alkoxy oxygen-centered radicals, such as those involving heteroatom-substituted oxygen (e.g., N−O•), have also found wide applications in synthesis due to their ease of oxidation and ability to provide a variety of products. For example, Chiba et al. has demonstrated that under heating in the presence of TEMPO, both oximes and hydrazones, which are easily obtained through carbonyl condensation, are prone to oxidation.[53]

2.1.1.7. C Radical. HAT mediated by C-centered radicals is rarer than its heteroatom counterparts. Unlike mechanisms initiated by N• and O•, where C−H bonds are exchanged for stronger N−H or O−H bonds,[54] the C• pathway faces the challenge that both the precursor and the product contain C−H bonds. Therefore, the necessary driving force for these transformations is required, as in the case of alkyl C−H HAT, which exchanges a C(sp^2)-centered group for a lower energy C(sp^3) group, thus forming a stronger aromatic C−H bond. In 1988, Curran et al.[55] first reported the transfer of the C• site between C−H bonds via intramolecular HAT (mechanism shown in Figure 3). This pioneering work promoted HAT from alkyl C−H to vinyl by utilizing the energy difference between C(sp^2) and C(sp^3) radicals. It is demonstrated that bromoethenyl could serve both as a radical precursor and an intramolecular trap, leading to the substituted cyclopentane product.[56] Additionally, Huang et al.[57] developed an efficient method for the trifluoromethylation of nitrogen heterocycles via copper-catalyzed intramolecular trifluoromethylation, showcasing the application of C(sp^2) radicals in trifluoromethylation reactions. Although C(sp^3)-radical-mediated HAT mechanisms are rare and highly challenging, there is still significant potential to design new strategies that promote the migration of C radicals between carbon atoms.

The selective functionalization of remote C−H bonds via intramolecular HAT is a breakthrough in organic synthesis. This radical-mediated approach complements closed-shell mechanisms and, with advancing mild radical generation methods, offers new opportunities for C−H functionalization. HAT reactions have significant advantages in organic synthesis, especially in terms of selective functionalization, mild

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conditions, and high efficiency. In comparison with nonradical pathways, radical-mediated HAT reactions can achieve selective functionalization of remote C−H bonds, a challenge for traditional synthetic methods. However, these reactions are characterized by strict geometric and thermodynamic constraints at the reactive sites, leading to diminished efficiency for certain substrates. In addition, the selection and efficiency of radical trapping agents play a critical role in determining the overall success of the reaction, further limiting its utility in the functionalization of complex, multifunctional molecules.

2.1.2. HAT Reactions without Free Radicals. HAT mechanisms offer superior selectivity in comparison with traditional radical-mediated processes by avoiding radical intermediates, leading to more controlled and selective reactions. These mechanisms, such as metal-catalyzed HAT and hydrogen bond-mediated transfer, enhance efficiency and selectivity, making them valuable in catalysis, organic synthesis, and molecular device design. Unlike traditional radical-mediated HAT reactions, nonradical HAT reactions do not rely on radical intermediates but instead achieve hydrogen atom transfer directly through hydrogen donors and acceptors. The core of this process involves efficient and mild hydrogen transfer via nonradical pathways, such as dynamic cleavage and formation of metal-hydride bonds,[30,31,58] hydrogen bonding networks,[32,33] and electron transfer-coupled hydrogen transfer (ET-HT) in photocatalytic and electrocatalytic reactions.[34,35,59] These methods avoid nonselectivity and by-product issues often associated with traditional radical reactions. Additionally, in molecules with hydrogen donor or acceptor characteristics[60] (e.g., borohydrides, silanes, or amine compounds), hydrogen atoms can be activated through coordination or specific catalytic systems, enabling diverse functionalization of chemical bonds via small-molecule mediation. The following sections will introduce these nonradical HAT pathways in detail.

2.1.2.1. Metal-Catalyzed Hydrogen Atom Migration. Metal-catalyzed hydrogen atom transfer is an important transformation in organic synthesis, involving the directional migration of hydrogen atoms facilitated by transition metal catalysts such as palladium (Pd), ruthenium (Ru), and rhodium (Rh). This process typically involves the formation and cleavage of metal-hydride bonds, with hydrogen migration occurring via metal-hydride intermediates, without generation of radical intermediates, thereby ensuring stereochemical and chemical selectivity in the reaction. Among metal-catalyzed HAT reactions, palladium-based catalytic systems have received particular attention and are widely used for the activation and functionalization of C−H bonds. For example, Pan et al.[31] reported a Pd(0)-catalyzed amination of inactivated C(sp^3)−H bonds, where C−N bond formation was achieved through hydrogen atom transfer. He et al. described a Pd(0)-catalyzed alkynylation of C(sp^3)−H bonds,[30] in which the C−H bond was activated and coupled with alkynyl halides via hydrogen atom transfer. These studies not only showcase the application of Pd-catalyzed C−H bond activation in synthetic chemistry, but also highlight the central role of HAT in the formation of new carbon−carbon and carbon-heteroatom bonds. Through these precisely controlled C−H activation reactions, scientists are able to efficiently construct complex organic molecules, which has far-reaching implications in fields such as drug development.

2.1.2.2. Concerted Transfer Mediated by Hydrogen Bonds. Under strong hydrogen bonding networks or similar multi-center interactions, hydrogen atoms are transferred from one group to another through concerted transfer, commonly observed in biomolecular systems or similarly designed molecular systems. Hydrogen bond-mediated concerted transfer plays a crucial role in enzyme-catalyzed reactions, often involving the simultaneous transfer of protons and electrons between donors and acceptors, thereby enabling effective tunneling effects. This is an important mechanism for achieving highly efficient and selective reactions.[33] For example, in lipoxygenase and dehydrogenase enzymes, HAT is precisely controlled through hydrogen bonding networks, enhancing both the efficiency and selectivity of the reaction. In the case of amino acid dehydrogenase, the relative positioning of the substrate and coenzyme NAD(P)H during catalysis determines the stereoselectivity of the enzyme. Similarly, covalent organic frameworks (COFs) interact with isopropanol through hydrogen bonding to promote isopropanol dehydrogenation and the transfer of hydrogen atoms between isopropanol and cinnamaldehyde, thus improving catalytic activity.[32] These findings demonstrate that hydrogen bond-mediated concerted transfer plays a central role in enzyme-catalyzed reactions, enabling efficient HAT in biological systems and providing a theoretical foundation for designing new artificial catalysts.

2.1.2.3. Electron Transfer Coupled with Hydrogen Transfer. Electron transfer coupled hydrogen transfer is an important mechanism in photocatalytic and electrocatalytic reactions, enabling the efficient transfer of hydrogen atoms from donors to acceptors by directly coupling hydrogen transfer with electron transfer. In this mechanism, the hydrogen atom and electron migrate in concert without generating of free radical intermediates, thus avoiding the nonselectivity associated with radical-mediated reactions. In photocatalysis, catalytic systems based on triplet−triplet energy transfer (TTEnT) induce hydrogen transfer from the donor to the acceptor through the interaction between the triplet-state sensitizer and substrate molecules. For example, Kleinman et al.[35] reported a [2π+2σ] photochemical addition reaction mediated by triplet energy transfer. In this process, excited-state molecules generated via photocatalysis reacted with various alkenes, which led to HAT and the formation of bicyclic[2.1.1]hexane (BCH) products, exhibiting a high functional group density and excellent stereoselectivity. In electrocatalytic systems, hydrogen atom migration is induced by the electric field in electrochemical reactions, enabling directional transfer. This reaction mechanism has been applied in selective reductions and molecular modifications. Gnaim et al.[34] successfully developed a cobalt-catalyzed electrochemical hydrogen atom transfer (e-HAT) method, which selectively generates transition metal hydride (TMH) species to achieve diverse functionalization of unsaturated carbon−carbon bonds. This method expands the possibilities for controlling chemical selectivity and reactivity, showing significant potential in the synthesis of complex molecules. These studies demonstrate the broad application of the ET-HT mechanism in photocatalytic and electrocatalytic reactions. They highlight the mechanism's high selectivity and efficiency, offering not only a green and sustainable method to organic synthesis but also new insights into the functionalization of complex molecules. The ET-HT mechanism holds significant potential in electrocatalytic applications. By directly coupling hydrogen transfer with electron transfer, it can avoid the generation of free radical

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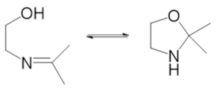
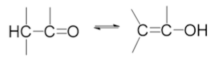
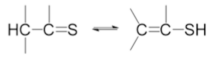
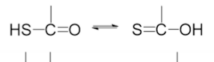
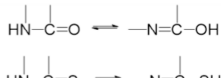
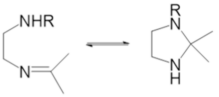
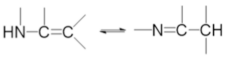
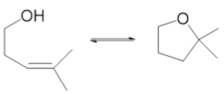
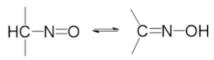
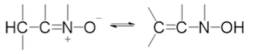
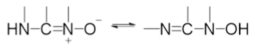
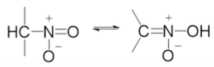
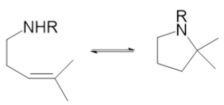
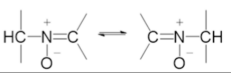
Table 1. Proton Transfer Reactions Involving Double Bond Shift or Cyclization[61]

Name of heterocycle	X	Y	Equilibrium	Name of prototropy	X	Z	Y	Equilibrium
tetrahydrooxazole	O	N		keto–enol	C	C	O	
				thione–enethiol	C	C	S	
tetrahydrothiazole	S	N		thiol–thione	S	C	O	
				amide–iminol	N	C	O	
tetrahydroimidazole	NR	N		thioamide–thioiminol	N	C	S	
				enamine–imine	N	C	C	
				amine–imine (amidine group)	N	C	N	
tetrahydrofuran	O	CH		nitroso–oxime	C	N	O	
				nitrone–*N*-hydroxyenamine	C	C	NO	
tetrahydrothiophene	S	CH		aminonitrone–*N*-hydroxyimine	N	C	NO	
				nitro–aci-nitro (nitro-nitrolic acid)	C	NO	O	
tetrahydropyrrole	NR	CH		Behrend rearrangement	C	NO	C	

intermediates, thereby enhancing the selectivity and efficiency of the reaction.

2.1.2.4. Small-Molecule-Mediated HAT. Molecules with hydrogen donor or acceptor properties, such as borohydrides, silanes, or amines, can directly participate in HAT without the need to form radical intermediates. Recent advancements in research have shown that photocatalytic strategies based on neutral Eosin Y can effectively achieve the stepwise functionalization of polyhydrosilanes, leading to the synthesis of fully substituted silicon compounds.[60] In these studies, Eosin Y photocatalysis facilitates the transfer of hydrogen atoms from silanes, which then react with various reagent chemicals to synthesize a range of functional silicon reagents. This process not only avoids the generation of radical intermediates but also enhances the atomic economy and step efficiency of the reaction. Through precisely controlled HAT reactions, scientists are able to efficiently construct complex organosilicon molecules, which have significant implications for fields such as materials science.

Overall, nonradical-mediated hydrogen atom transfer provides an efficient, mild, and selective tool for organic chemistry. Although its study is not as developed as that of radical-mediated HAT reactions, it holds significant importance in fields such as metal catalysis, organic synthesis, and photocatalysis/electrocatalysis. Future research can focus on the design of catalysts, in-depth exploration of reaction mechanisms, and further control of reaction pathways, which will offer new insights for the development of novel catalytic systems and functional molecules. Nevertheless, these reactions typically rely on specific substrate structures or functional groups to facilitate the transfer process, thereby restricting their general applicability to complex molecular systems.

2.2. Intramolecular Proton Transfer

Intramolecular proton transfer (IPT) refers to the process in which a hydrogen atom, as a proton (H^+), migrates between different functional groups within the same molecule. This phenomenon is crucial to a range of essential biological mechanisms. Proton transfer is linked to several significant processes, including the photoisomerization of dyes at low temperatures, phase transitions in ferroelectrics, the visual process, proton pumping across biological membranes, and various chemical and biochemical catalytic systems. The efficiency of this process often relies on the hydrogen bond network within the molecule. Hydrogen bonding networks play a crucial role in proton transfer in biological systems. These networks provide a structured pathway that enable efficient proton migration between donor and acceptor sites. They facilitate the concurrent transfer of protons and electrons, achieving an effective tunneling effect critical for enzymatic reactions. Hydrogen bonds serve as a conduit for proton transfer, facilitating the movement of protons. Moreover, proton transfer can induce alterations in the molecular electronic structure, such as changes in charge distribution and the shape of the electron cloud, which in turn influence the chemical properties of the molecule. Key mechanisms involved in intramolecular proton transfer include Ground-State Proton Transfer (GSPT), ESIPT, and Proton-Coupled Electron Transfer (PCET). In the following sections, we will provide an in-depth introduction to the mechanisms of intramolecular proton transfer and examine the latest advancements in research related to these reactions.

2.2.1. Ground-State Proton Transfer. GSPT involves the migration of protons through intramolecular hydrogen bonds within the ground state of a molecule. This process is often accompanied by tautomeric reactions, such as keto−enol

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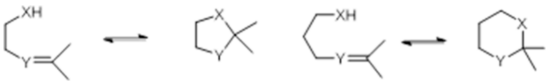
tautomerism and intramolecular cyclic proton migration. A notable feature of GSPT is its low energy barrier, which makes it readily achievable in both solution and solid-state environments.

2.2.1.1. Keto–Enol Tautomerism. Tautomerism in ambidentate compounds can be articulated using a general eq 1. When G is hydrogen, this process is known as "keto–enol tautomerism" or simply "keto–enol isomerism". In this framework, the proton transfer process generally involves the movement of protons from acidic groups such as –OH, –SH, –NH, or –CH to basic atoms like O, S, N, or C. In noncyclic conjugated systems, the delocalization of π electrons enhances the migration of hydrogen atoms between atoms X and Y. This migration takes place through various tautomeric forms, as shown in Table 1, and can be observed in compounds such as enol-ketones, thiocarbonyl-ene thiols, and amide-imino alcohols. Importantly, when a conjugated spacer exists between X and Y, tautomerism can still take place even if the two atoms are not directly adjacent. Keto–enol tautomerism, being the most prevalent and extensively studied example, typically arises in compounds that contain at least one carbonyl group alongside a sp^3 hybridized carbon atom, which is connected to the carbonyl and has multiple hydrogen atoms attached.[61]

$$GX–Z{=}Y \rightleftharpoons X{=}Z–YG \quad (1)$$

2.2.1.2. Intramolecular Cyclic Proton Migration. When a ring replaces the double bond between Y and Z, this reversible isomerization is referred to as "cyclic chain tautomerism" (eq 2). An example of this can be seen in the cyclization and ring-opening of aldoses, such as glucose, during mutarotation. In this isomerization process, both tautomers are stable enough to be distinguished by spectroscopy. The proportion of the two tautomers largely depends on the electronic effects of the substituent R′. Additionally, due to their smaller molecular size and higher ring tension, five-membered rings may have higher energy. Consequently, the ring closure of five-membered heterocycles is relatively unfavorable compared to six-membered heterocycles.[62]



(2)

2.2.2. Excited-State Intramolecular Proton Transfer. The primary mechanism of ESIPT involves the migration of a proton from the donor to the acceptor through intramolecular hydrogen bonds after the molecule has been excited by light or another energy source. This migration leads to changes in the molecular structure in the excited state. A key characteristic of ESIPT is that it is entirely reversible, resulting in significant alterations to the excited-state lifetime and fluorescence properties. In 1955, it was first reported that salicylic acid and other ortho-hydroxy acids and esters exhibit a pronounced Stokes shift, distinct from that of similar substances.[63] This observation led to the hypothesis that isomerization between enol and ketone forms occurs directly in the excited state through proton transfer, which is the essence of the ESIPT process (Figure 4a). As an important mode of structural tautomerism, ESIPT has been extensively studied and applied across various fields.

The ESIPT process requires the presence of proton donors (such as –OH and $-NH_2$) and proton acceptors (such as –C = O and –N =) within the molecule, as well as the capacity to form intramolecular hydrogen bonds between them. This

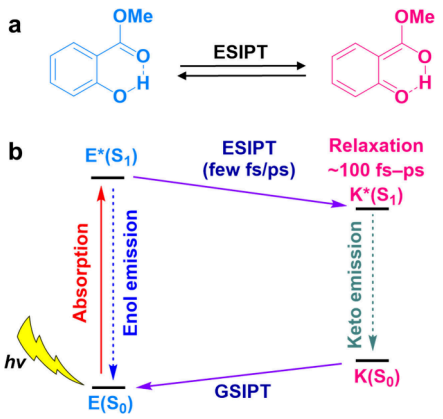


Figure 4. Mechanism and examples of ESIPT reaction. (a) The structure of methyl salicylate and its proton transfer isomers. Reproduced from ref 63. Copyright 1955 Springer Nature. (b) Schematic diagram illustrating the ESIPT mechanism. Reproduced from ref 5. Copyright 2016 The Royal Society of Chemistry.

unique process involves four distinct stages, illustrated in Figure 4b. In the electronic ground state, the fluorescent group typically exists in the enol form, stabilized by intramolecular hydrogen bonds. When the molecule is excited by light, it transits to the excited-state enol form (E*). Some of these molecules return to the ground state through a radiative transition, emitting enol fluorescence. Others undergo photoisomerization, transforming from the enol form (E) to the excited ketone form (K*). This transformation is driven by the redistribution of electronic charge during light excitation ($k_{ESIPT} < 10^{-12}$ s). The molecule in the K* form can also revert to the ground state ketone (K) via a radiative transition, emitting lower-energy ketone fluorescence. Since the ketone form is not thermodynamically stable, the molecule will eventually return to the original enol form through a reverse proton transfer (RPT) process. This unique four-level cycle (E → E* → K* → K) endows ESIPT fluorophores with diverse luminescent properties and adjustable luminescence mechanisms, indicating a wide range of potential applications.[5] The ESIPT mechanism has various reaction characteristics that enable its application in multiple fields: 1. Due to the sensitivity of the ESIPT process to the surrounding medium, it is utilized for fluorescence probes.[64] 2. Because of the ESIPT process's responsiveness to external stimuli, it serves as a sensor.[65] 3. The dual fluorescence emission and broad half-peak width of ESIPT make it suitable for developing luminescent materials.[66] 4. ESIPT dyes exhibit significant fluorescence in the solid state and are applied in organic optoelectronic materials,[7] photo stabilizers,[67] molecular switches,[68] bioimaging,[8] and other areas. The following sections will provide detailed insights into these applications.

Researchers have leveraged the sensitivity and rapid response of the ESIPT process to develop fluorescence probes.[64] For example, Gu et al. synthesized a water-soluble ESIPT fluorescent probe known as 2-((4-((*tert*-butyldiphenylsilyl)oxy)-1,3-dioxoisoindolin-2-yl)methyl)-1-ethylpyridin-1-ium iodide (SPI), specifically designed for monitoring fluoride ions. In this probe, the presence of a *tert*-butyl diphenylsiloxy group protects the hydroxyl group, which in turn hinders the ESIPT process. However, when fluoride ions are present, they can cleave the *tert*-butyl diphenylsiloxy group, thereby releasing the fluorophore and

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resulting in fluorescence. This probe offers several advantages, including high selectivity, rapid response time, good water solubility, and a large Stokes shift. Additionally, it can be used for the quantitative determination of fluoride ions.

The response of the ESIPT process to external stimuli makes it a promising basis for developing various new sensors. Su et al. prepared an ultrafast (responses in seconds) and highly selective water photoluminescence (PL) sensor using microporous Zn-MOF (metal−organic framework) materials.[65] This sensor is capable of detecting moisture with a sensitivity to 1% relative humidity or 0.05% volume ratio. The composition of this Zn-MOF is $Zn(hpi_2cf)(DMF)(H_2O)$, which is formed from the double-emission ligand 5-(2-(5-fluoro-2-hydroxyphenyl)-4,5-bis(4-fluorophenyl)-1*H*-imidazol-1-yl) isophthalic acid (hpi_2cf), known for its characteristic ESIPT behavior. The sensor operates by facilitating the transformation between the hydrated and dehydrated phases through the reversible coordination of water molecules in the ligand. This mechanism activates or deactivates the ligand's ESIPT process, effectively creating a dual-color photoluminescence switch. Potential applications for this sensor include detecting humidity in gases, trace water in organic solvents, thermography, and thermometers, among others.

The study of dual fluorescence emission and the broad half-peak width characteristics of ESIPT is significant for developing various new luminescent materials. In these systems, the enol form of the molecule typically generates short-wavelength blue light emission, while the ketone form emits long-wavelength green or yellow light. The combination of the spectra from these two forms can produce white light. Thus, the ability to regulate enol and ketone emissions allows a single ESIPT system to cover the entire visible light spectrum, making it critical for producing white light. Chou et al. synthesized three new ESIPT molecules based on 7-hydroxy-1-indenone. By incorporating benzene and naphthalene rings, they achieved near-white light emission in the solid state.[69] Additionally, organic light-emitting diodes (OLEDs) were successfully developed using naphthalene-modified molecules, demonstrating that white light can be produced using a single ESIPT system. Furthermore, there is potential to create innovative ESIPT devices that emit all colors across the visible light spectrum. Park et al. introduced a general strategy for the wide-spectrum regulation of imidazole-based ESIPT materials, employing three different approaches:[70] introducing node-plane models, extending effective conjugation lengths, and modifying heterocycles. This research revealed that the molecular structure can yield strong photoluminescence of varying colors throughout the visible light range, specifically from 450 to 630 nm. The studies examining the impact of the system's conjugated structure and aromaticity on ESIPT and dual fluorescence emission are crucial for designing ESIPT molecules. Fine-tuning the energy levels of the two excited states to establish excited-state equilibrium offers a promising avenue for further research into multiple fluorescences.

Most substances exhibit weak fluorescence effects in their crystalline states. However, ESIPT dyes demonstrate significant ESIPT effects even in the solid state.[71] This characteristic broadens the application prospects for ESIPT dyes. Single-crystal ESIPT materials, due to their high uniformity, facilitate more efficient proton transfer processes in the excited state, resulting in higher fluorescence quantum efficiency. Jang et al. synthesized a new imidazole-based ESIPT material and investigated its amplified spontaneous emission (ASE) characteristics. These materials include hydroxy-substituted tetraphenyl imidazole (HPI) and its propionate derivative HPI-Ac. By incorporating four phenyl groups on the imidazole ring, they optimized intramolecular interactions, thereby enhancing fluorescence quantum efficiency and ASE performance.[72] Furthermore, controlling the molecular arrangement allows for the adjustment of luminescence performance in polycrystalline forms of ESIPT phosphors. The aggregation-induced emission/aggregation-induced emission enhancement (AIE/AIEE) mechanism is also employed to improve the fluorescence quantum efficiency of solid-state ESIPT emitters. By restricting intramolecular rotation and twisting intramolecular charge transfer mechanisms, the fluorescence intensity and quantum efficiency can be significantly enhanced in the solid state.[73] These advancements provide essential theoretical foundations and practical guidance for the future development of high-performance solid-state luminescent materials.

Despite its unique photophysical properties, the ESIPT process faces significant challenges in practical applications. Its excitation and emission wavelengths are largely confined to the UV and visible regions, limiting tissue penetration and deep imaging capabilities. Current ESIPT fluorescent probes also struggle with sensitivity, selectivity, photostability, and cell membrane permeability. In addition, their narrow design concepts hinder the adaptability to complex biological systems, restricting broader adoption of the ESIPT technology.

2.2.3. Proton-Coupled Electron Transfer. Marcus theory, which describes the kinetics of electron transfer processes, has been applied to predict the rate constants of HAT reactions and optimize PCET reaction rates and selectivity in both biological and synthetic systems.[36] PCET reactions are essential processes for energy conversion that occur widely in both natural and artificial systems. These reactions are usually facilitated by external fields (such as electric and light fields) or catalysts, with protons and electrons transferring cooperatively.[74] There are two main mechanisms for these reactions: the stepwise mechanism and the concerted mechanism.[75] In the stepwise mechanism, electron transfer (ET) and proton transfer (PT) occur separately, with intermediates involved. The specific order of electron and proton transfer depends on the system in question.[76] For example, Zhang et al. reported in 2024 on a hexaazatriphenylene (HATNA) molecular switch, demonstrating a PT-ET mechanism in which proton transfer occurs before electron transfer.[77] In the same year, Kessinger et al. used nanosecond transient absorption spectroscopy to analyze the kinetics at the PCET reduction reaction interface, confirming the ET-PT mechanism in which electron transfer occurs before proton transfer.[78] In contrast, the concerted mechanism involves the simultaneous transfer of protons and electrons. This coupling can provide an additional driving force, reducing the activation energy of the reaction and making it proceed more easily. For example, Zhu et al. found that altering the surface structure of the reaction site affected the activity of the deprotonation process. Surfaces with higher concerted transfer efficiency exhibit higher activity in the oxygen evolution reaction (OER).[79] In practice, these two mechanisms are not strictly opposed; they can coexist or transform under certain conditions.[80]

Current research on PCET reactions has made significant advances in both theoretical and experimental aspects. On the theoretical side, R.A. Marcus developed a theory, known as

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Marcus theory, to describe the kinetics of electron transfer reactions. Marcus theory is applicable not only to adiabatic electron transfer reactions but is also extended to nonadiabatic reactions through quantum mechanical methods, providing a solid theoretical foundation for understanding and designing electron transfer processes. Building on Marcus theory, Bolton et al. proposed a simplified model to predict the rate constants of HAT reactions within the PCET framework. This model focuses on the free energy changes and intrinsic energy barriers of reactions, utilizing the Marcus cross relation to integrate experimental data with theoretical predictions. Their approach demonstrates broad applicability and accuracy in estimating HAT reaction rates across various reactants and solvents.[81] On the experimental front, researchers are optimizing the rate and selectivity of PCET by introducing functional groups and modifying molecular structures. For example, the design of molecules with appropriate hydrogen bonding networks and conjugated systems can enhance the coupling of protons and electrons.[82] Additionally, advanced techniques such as ultrafast spectroscopy and single-molecule fluorescence imaging are employed to capture the dynamics of PCET.[83] By mimicking the mechanisms of natural enzymes through intramolecular PCET, valuable insights are provided for the development of biomimetic catalysts.[36] The PCET process plays a crucial role in chemistry and biochemistry, but its slow kinetics in neutral and alkaline environments hinder the industrial applications. In addition, the process has limited substrate and reaction selectivity, with most research focusing on specific substrates while activation methods for others remain underexplored. These challenges pose significant obstacles to the broader practical implementation of PCET. Overall, as the theoretical framework for PCET deepens and experimental techniques continue to evolve, this field is poised for broad application prospects.

2.3. Intramolecular Hydride Transfer

The migration of hydride anions within molecules is a key topic in organic chemistry, particularly in the construction of complex molecular structures and organic synthesis. This process typically involves the migration of a hydride, along with its bonding electrons, to an electron-deficient center within the molecule, resulting in the formation of more stable intermediates. These intermediates are often further stabilized by charge delocalization or conjugation effects, which provide active sites for subsequent intramolecular reactions. As a result, hydride migration can be observed in many rearrangement reactions and in the synthesis of heterocyclic compounds through [1,*n*]-hydride transfer/cyclization. The following sections will discuss these processes in detail.

2.3.1. Carbocation Rearrangement. The migration of hydride anions demonstrates unique advantages in the construction of complex molecular frameworks, particularly in the synthesis of heterocyclic structures, making it an effective route for achieving efficient organic synthesis. The driving force behind this migration primarily stems from the formation of more stable intermediates. For example, the stability of different types of carbon cations follows this order: tertiary carbon cation > secondary carbon cation > primary carbon cation > methyl cation. Therefore, the tendency to form more stable ionic structures is one of the key driving forces for hydride migration.

Typical hydride anion migration reactions include rearrangement reactions of carbon cations, such as the Wagner-Meerwein rearrangement and the Demyanov rearrangement. These reactions share a common feature: the migration of hydride anions stabilizes the carbon cation while simultaneously rearranging the molecular structure. The Wagner-Meerwein rearrangement stabilizes the carbon cation through hydride transfer, leading to the reorganization of the molecular skeleton and the formation of complex cyclic or branched structures. This type of reaction is particularly crucial in the synthesis of complex organic molecules, often employed to enhance molecular diversity and optimize the properties of target molecules. The Demyanov rearrangement, on the other hand, involves hydride migration while the carbon cation interacts with imines to generate new amine compounds, and is widely used in the synthesis of amine-based chemicals.

In industrial applications, the advantages of hydride anion migration are significant. For example, in the catalytic cracking of petroleum, carbon cations often undergo intramolecular rearrangements, including hydride migration, to form more stable carbon cations. This rearrangement process aids in the cleavage of heavy oil molecules into more valuable lighter components, significantly improving the efficiency of catalytic cracking.[84]

2.3.2. [1,*n*]-Hydride Transfer/Cyclization. The [1,*n*]-hydride transfer/cyclization method enables the activation of remote C(sp^3)−H bonds, facilitating the construction of various important heterocyclic compounds. This approach holds significant potential for applications in fields such as medicinal chemistry, natural product synthesis, and materials science, offering new avenues for the development of diverse bioactive molecules and functional materials.[37−42] Through the [1,*n*]-hydride transfer/cyclization strategy, various natural products and bioactive molecular frameworks have been successfully synthesized, such as tetrahydroquinoline[85,86] and chromene,[87,88] among others.

In the [1,*n*]-hydride transfer/cyclization reaction, the substrate typically consists of two parts: the "hydride donor" and the "hydride acceptor." The hydride donor is usually a tertiary amine, ether, or alkyl group, while the hydride acceptor is often an electron-deficient double or triple bond, including compounds such as alkenes, alkynes, aldehydes, ketones, and imines. Under acidic catalytic or heated conditions, the hydride is transferred from the donor to the acceptor, forming a zwitterionic intermediate, which then undergoes intramolecular cyclization to generate the corresponding cyclic compound, as shown in the mechanism in Figure 5a. Notably, during the hydride transfer process, the hydride donor is oxidized, and the hydride acceptor is reduced; however, no overall redox reaction occurs. Therefore, this process is also referred to as "hydride transfer/cyclization" or "intramolecular redox relay".

In hydride transfer/cyclization reactions, the structural diversity of hydride donors and acceptors leads to a variety of chemical bond types, ultimately enabling the construction of different types of heterocyclic frameworks. Among them, tertiary amines are widely used as hydride donors.[6,38,40,41] This type of reaction is often summarized as the "*tert*-amino effect", through which various nitrogen-containing heterocyclic frameworks can be constructed. Specifically, the *tert*-amino effect refers to a unique intramolecular cyclization mechanism in *N*,*N*-disubstituted aromatic tertiary amines with adjacent conjugated electron-deficient structures. The rate-determining step in this process is the migration of a hydrogen atom, which transfers from the nonactive methylene group at the α-position of the tertiary amine to the conjugated double bond structure

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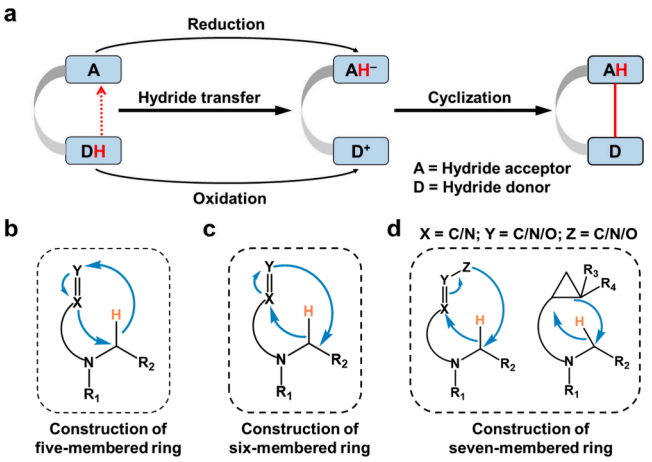

Figure 5. (a) Mechanism of the [1,*n*]-hydride transfer/cyclization reaction, and the hydride transfer reaction mechanisms for the formation of (b) five-membered, (c) six-membered, and (d) seven-membered heterocyclic compounds.

(such as conjugated electron-deficient alkenes, carbonyls, imines, nitro groups, etc.). After migration, the system tends to form a more stable iminium cation. This reaction facilitates the construction of complex nitrogen-containing heterocyclic frameworks and provides a powerful method for synthesizing biologically active and structurally complex molecules.[6,89]

Additionally, researchers can construct a variety of novel heterocyclic compounds using this strategy by manipulating the substrate structure. Based on the ring size of the cyclization products, these heterocycles can be divided into four categories: five-membered,[90−92] six-membered,[93−95] seven-membered,[96,97] and medium-sized[98−100] spiro- and fused-ring compounds, all of which are constructed via C(sp^3)−H functionalization. Figure 5 illustrates the hydride transfer reaction mechanisms for the formation of five-membered (b), six-membered (c), and seven-membered (d) heterocyclic compounds. Examples will be presented sequentially below.

The construction of five-membered ring molecules is typically achieved through C(sp^3)−H bond functionalization, which often involves [1,4] or [1,5]-hydride transfer, followed by [1,5]-cyclization to form the target molecule. For example, in 2018, Mori et al. proposed a strategy based on continuous hydride transfer and successfully synthesized various indole derivatives.[92] The method uses ortho-substituted aminobenzoyl esters as substrates, where, under titanium ion catalysis, the classic [1,5]-hydride transfer first occurs, generating an iminium ion intermediate. Subsequently, due to the nucleophilicity of the ester group at the α-position, a [1,5]-cyclization occurs at the benzylic position, forming the indole framework. Further acid-catalyzed dehydroxylation produces another iminium ion intermediate. At this stage, when R' is hydrogen, the intermediate undergoes [1,2]-hydride transfer and aromatization, yielding 3-ester-substituted indole derivatives. When R' is alkyl, the intermediate undergoes [1,2]-hydride transfer, decarboxylation, and aromatization, forming 3-alkyl-substituted indoles. This strategy provides an innovative approach for the efficient synthesis of indole-based structural units.

The reaction for constructing six-membered rings via C(sp^3)−H functionalization typically involves a sequence of steps such as [1,5]-hydride transfer/[1,6]-cyclization, or [1,6]-hydride transfer/[1,5]-cyclization/[1,2]-migration. For example, in 2019, Wang et al. reported a strategy based on $B(C_6F_5)_3$-catalyzed [1,5]-hydride transfer/cyclization.[95] In this reaction, $B(C_6F_5)_3$ acts as a hydride acceptor, receiving the hydride from the carbon adjacent to the nitrogen in the substrate, forming a boron hydride species, while the substrate forms an iminium ion intermediate. This intermediate then undergoes cyclization, generating a carbon cation intermediate. Subsequently, the carbon cation receives a hydride from the boron hydride species, ultimately forming the tetrahydroquinoline framework. Notably, the substrate does not contain a classical hydride acceptor; instead, $B(C_6F_5)_3$ catalyzes the reaction as a hydride mediator. This strategy offers a new approach for hydride transfer/cyclization reactions and holds significant research implications.

The reaction for constructing seven-membered rings via C(sp^3)−H functionalization typically involves a sequential process of [1,5]-hydride transfer and [1,7]-cyclization. In 2019, Mori et al. successfully synthesized complex nitrogen-containing tricyclic fused structures using a continuous cyclization strategy based on the *tert*-amino effect.[97] With $Yb(OTf)_3$ as the catalyst, the reaction first undergoes [1,7]-hydride transfer/cyclization to construct the fully carbon-containing seven-membered ring structure. This is followed by [1,5]-migration/cyclization to form the piperidine ring, efficiently constructing the nitrogen-containing tricyclic fused system with high yield and diastereoselectivity. When the carbon chain of the tertiary amine is extended, the reaction proceeds through [1,7]-hydride migration to generate an eight-membered ring, also exhibiting good yield and diastereoselectivity.

Significant progress has been made in controlling intramolecular hydride transfer for the synthesis of heterocyclic compounds, particularly through the [1,*n*]-hydride transfer/cyclization method. This method enables the activation of remote C(sp^3)−H bonds, facilitating the construction of various important heterocyclic compounds. Therefore, the [1,*n*]-hydride transfer/cyclization strategy exhibits remarkable step efficiency and superior atomic economy. The method is operationally straightforward, requiring only Brønsted or Lewis acid catalysis, or even simple thermal activation, to drive the reaction. This approach provides significant versatility and flexibility in the synthesis of natural products and the construction of bioactive molecular frameworks, offering valuable insights for the precise and efficient synthesis of heterocyclic compounds.

Hydride migration typically requires specific acidic or alkaline conditions, limiting its applicability to sensitive substrates. Side reactions during migration can compromise product selectivity and purity, while controlling the migration pathway in complex molecular systems remains challenging. Therefore, precise regulation of reaction conditions is crucial to improving the efficiency and selectivity of hydride migration in practical applications.

2.4. Intermolecular Hydrogen Transfer

Intermolecular hydrogen transfer primarily involves processes such as hydrogen atom transfer, proton migration, hydrogen anion transfer, and catalyzed transfer hydrogenation reactions. These types of reactions play a significant role in various fields, including chemical synthesis, environmental monitoring, and food safety detection. This section will briefly explore the process of intermolecular hydrogen transfer, using hydrogen atom transfer and proton migration as examples.

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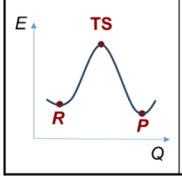
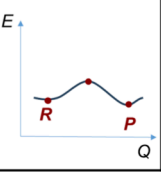
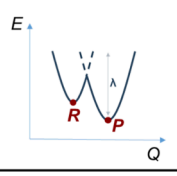
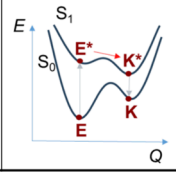
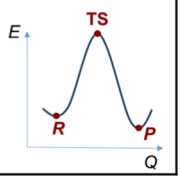
Table 2. Potential Energy Surfaces for Different Hydrogen Transfer Pathways

H•		H⁺		H⁻
radical-mediated HAT	non-radical HAT	ground-state proton transfer	ESIPT	hydride transfer
				

In recent years, advancements in photocatalysis have significantly boosted research into intermolecular HAT reactions. Photocatalysts can extract hydrogen atoms directly from donor molecules while in an excited state, leading to the formation of active intermediates that transfer hydrogen atoms to acceptor molecules, thus initiating the reaction cycle.[101] Effective photocatalysts for this process include aromatic ketones and polymetallic oxoanions. Additionally, indirect HAT methods enhance the process by introducing specific species that generate thermodynamic hydrogen abstractors. These methods include SET, energy transfer, and ligand-assisted PCET processes.

Proton transfer can occur within or between molecules. Intramolecular proton transfer may take place in isolated molecules in the gas phase at very low pressures or in highly diluted solutions of nonproton solvents.[102] In contrast, intermolecular proton transfer can happen in concentrated nonproton solutions, argon matrices, or lattice structures, where dimers, trimers, and other aggregates might form. These aggregates can be stabilized by intermolecular hydrogen bonding and can consist of either the same tautomeric molecules or different tautomeric forms.[103] Polar proton solvents, such as water or alcohols, can engage in proton transfer by forming cyclic or linear complexes with tautomers.[104] The structure of these complexes depends on the conformation and configuration of the tautomers involved. In strong polar nonproton solvents, the presence of acids or bases can lead tautomeric molecules to lose or gain a proton, resulting in corresponding meso-anions or cations. These meso-anions or cations can then gain or lose a proton, respectively, to create new tautomeric forms.[105] In all these cases, the conjugation within the tautomeric part facilitates proton transfer. Additionally, protons can migrate within framework structures, such as COFs[106] and MOFs,[107] enabling the creation of proton conductors. These structures feature highly adjustable pores and good stability, making them particularly advantageous for use in proton-conducting materials. By introducing proton donor functional groups or external proton sources into the framework structure, the proton conduction performance can be optimized. As two fundamental mechanisms of hydrogen transfer, hydrogen atom transfer, and proton migration play essential roles in chemistry and biochemistry. They also serve as the foundational research for specialized hydrogen transfer mechanisms, such as ESIPT. Table 2 compares the potential energy surface changes of different hydrogen transfer pathways. The potential energy surface of hydrogen atom transfer mediated by free radicals has a unimodal peak because free radical recombination needs to cross a large energy barrier,[4] while the potential energy surface of hydrogen atom transfer mediated by nonfree radicals reduces the reaction energy barrier through a cooperative mechanism,[33] so the potential energy surface is relatively flat. The ground-state proton transfer conforms to Marcus theory, where the potential energy surface is symmetric or asymmetric double well, and the height of the energy barrier is related to solvent recombination. The ESIPT pathway has a special four-level mechanism,[5] and the molecules can undergo rapid proton transfer in the excited state. Finally, due to overcoming the strong electronegativity and steric hindrance of hydride transfer,[6,89] the potential energy surface is similar to that of free radical mediated hydrogen migration, but the energy barrier is higher.

3. HYDROGEN TRANSFER IN MOLECULAR DEVICES

Incorporating hydrogen transfer reactions into molecular devices introduces a novel approach to advancing reaction kinetics and molecular electronics. These reactions enable precise modulation of molecular geometry, electronic configuration, and charge transport properties, thereby offering a broad range of functional responses, particularly relevant to molecular switching, sensing, and optoelectronic applications. Furthermore, highly sensitive electrical detection in molecular devices provides a platform for monitoring the kinetics of hydrogen transfer reactions and regulating and optimizing reaction pathways. Proton transfer, in particular, exhibits distinct physicochemical properties, including high chemical stability, reversibility, and efficient structural modulation—key features essential for achieving nuanced functional modulation. Therefore, the proton transfer process plays a dominant role in the study of hydrogen transfer within devices, and the following sections will focus on this aspect. Molecular devices based on proton transfer encompass various microstructures, ranging from zero-dimensional (0D) single-molecule devices[11,16,108] to two-dimensional (2D) molecular membrane devices[18,109−111] and three-dimensional (3D) COF devices.[29,112] Remarkable progress has been achieved in these devices for molecular switching,[13,21,23,113−115] sensing,[23,25] and optoelectronics,[25,116−119] ferroelectrics,[110,111,120] and stimuli-responsive color-changing applications.[28,121,122] This section focuses on the design, mechanisms, and functional applications of 0D, 2D, and 3D molecular devices based on proton transfer, providing a comprehensive summary of the key advancements.

3.1. Single-Molecule Devices

Single-molecule devices, crucial in molecular electronics, have attracted significant attention due to their ultrasmall size, tunable electronic behaviors, and unique physicochemical properties.[12,20,24,108,115,123] By utilizing individual molecular characteristics, these devices can surpass conventional counterparts, promoting advancements in nanoelectronics, molecular sensing, and functional materials. Introducing proton transfer

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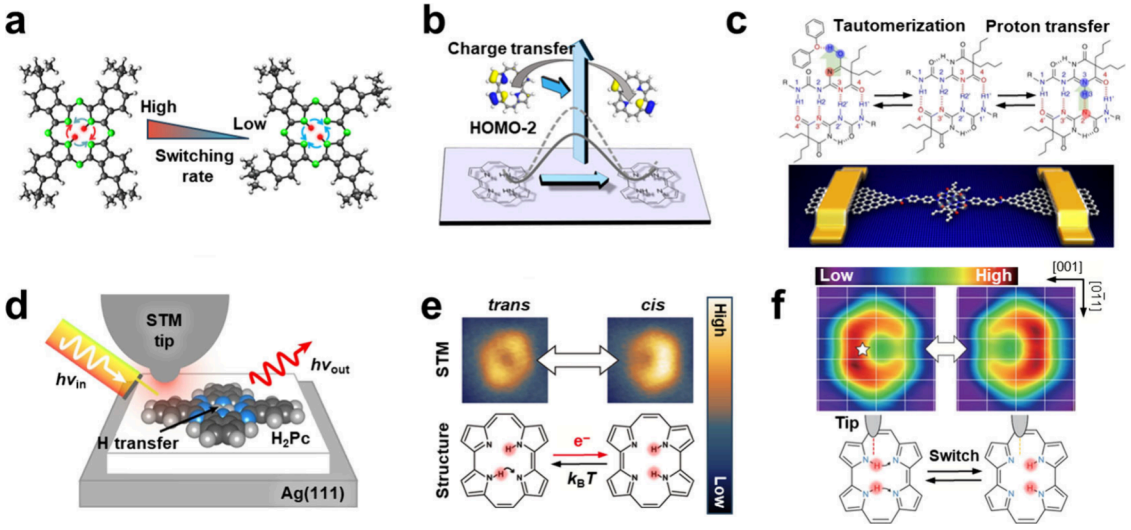

Figure 6. Mechanisms and factors of proton transfer-based single-molecule devices. (a) Effect of substituents on tautomerism in proton transfer reaction of tetra-*tert*-butyl phthalocyanine. Reproduced from ref 124. Copyright 2018 American Chemical Society. (b) Important role of charge transfer in HOMO−2 orbital transformation of the porphin molecule. Reproduced from ref 10. Copyright 2019 American Chemical Society. (c) Random rearrangement of hydrogen bonds in a monomolecular junction bridged by a quadruple hydrogen bond dimer of UPy. Reproduced from ref 16. Copyright 2018 Springer Nature. (d) Photoisomerization of free radical phthalocyanine is controlled by local plasma field. Reproduced from ref 108. Copyright 2024 Springer Nature. (e) Reversible tautomerization of single porphyrins is controlled by temperature and electric field. Reproduced from ref 11. Copyright 2015 American Chemical Society. (f) Force-induced tautomerism of single porphyrin molecules. Reproduced from ref 12. Copyright 2016 Springer Nature.

into single-molecule devices facilitates molecular isomerization, bond rearrangement, and electron redistribution, offering precise modulation of molecular properties under various stimuli. This process has advanced single-molecule devices for switching, relaying, and luminescence. This section highlights recent progress in proton transfer-based single-molecule devices, emphasizing their mechanisms and applications.

3.1.1. Overview of Proton Transfer in Single-Molecule Devices. Complex intramolecular interactions and external conditions make it challenging to predict and control selective hydrogen transfer pathways and mechanisms. To explore the factors influencing intramolecular proton transfer, Leisegang et al. utilized low-temperature scanning tunneling microscopy to study proton transfer in *tert*-butyl-substituted phthalocyanine isomers on Ag(111).[124] The *tert*-butyl groups alter the proton transfer behavior due to steric hindrance, which weakens the molecule−surface coupling. By correlating proton transfer barriers with intramolecular bond lengths, they developed an energy landscape model that explains variations in tautomerization rates. The spacing of the *tert*-butyl groups influences macrocycle bending and the height of the proton transfer barrier[124] (Figure 6a). In addition to the effects of substituents, internal molecular orbitals are identified as another key factor influencing intramolecular proton transfer. Li et al. studied porphyrin adsorption and tautomerization on transition metal surfaces. High hydrogen tautomerization barriers on Pt(110) were found to control state transitions at high temperatures. They demonstrated that porphyrins switches between two states on Pt(110) at ambient temperature, which is linked to charge transfer involving the HOMO−2 orbital[10] (Figure 6b).

Several studies have also explored the impact of external factors on proton transfer. A hydrogen-bridged single-molecule junction is employed to investigate the effects of temperature and solvent on hydrogen bonding dynamics, revealing a multimodal distribution[16] (Figure 6c). Ladenthin et al. employed STM to investigate temperature- and force-induced isomerization in porphyrin molecules on Cu surfaces, demonstrating the ability to control isomerization through temperature and force[11,12] (Figure 6e,f). Furthermore, scanning tunnelling microscope break junction (STM−BJ) is used to study the electronic properties and photoconductivity of SMe−PhOH under light illumination, highlighting the influence of ESIPT on the molecular properties.[125] STM−BJ is also employed to study the kinetics of amino group protonation at metal-solution interfaces, revealing reversible reaction mechanisms and the regulation of force.[126] Rosławska et al. used localized plasmonic fields to control photoisomerization in phthalocyanine, tuning reaction rates and conformational populations[108] (Figure 6d). In a recent study, STM and pump−probe techniques are employed to control hydrogen proton transfer within phthalocyanine molecules on Ag substrates, offering new opportunities for manipulating proton dynamics at the molecular level.[127] Building on prior studies, electric-field-induced hydrogen atom transfer in H_2Pc is studied, with observations showing increased reaction rates as the field strength was increased.[128] The investigation of factors influencing proton transfer in single-molecule devices has significantly advanced our understanding of the underlying mechanisms. This progress paves the way for the precise regulation of proton transfer, which is crucial for the development of single-molecule proton transfer technologies.

3.1.2. Single-Molecule Proton Transfer Switching Devices. IPT and related processes can influence molecular configurations, electronic states, and charge transport properties, playing a vital role in enabling functional responses in molecular switches, sensors, and optoelectronic applications. Building on well-established mechanisms for controlling proton transfer processes in single-molecule devices, various single-molecule switching devices are successfully developed. These devices enable circuit switching by forming different conductance states through proton-induced changes in trans-

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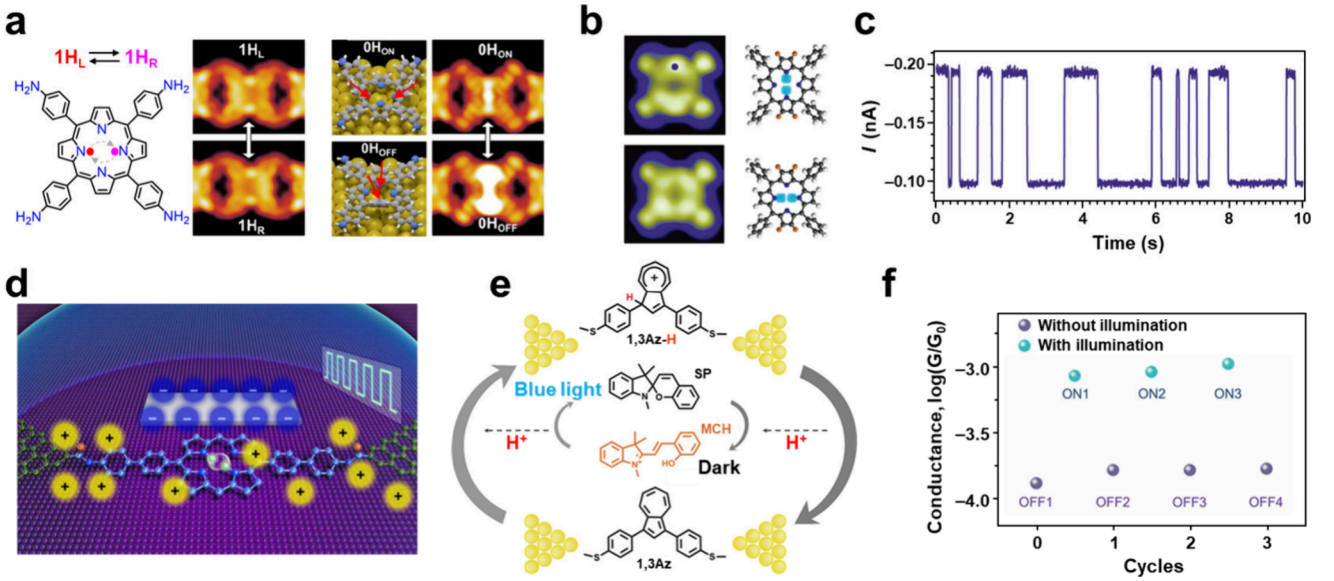

Figure 7. Single-molecule switching device based on proton transfer. (a) Binary proton transfer in TAPP molecular chains. Reproduced from ref 19. Copyright 2020 American Chemical Society. (b, c) Single proton transfer conductance switch based on free radical tetraphenyl porphyrin molecule. Reproduced from ref 20. Copyright 2012 Springer Nature. (d) Graphene-porphyrin-graphene single-molecule junctions operating in two configurations. Reproduced from ref 13. Copyright 2022 American Association for the Advancement of Science. (e, f) Construction of light-driven single molecule switch and logic gate. Reproduced from ref 22. Copyright 2019 John Wiley and Sons.

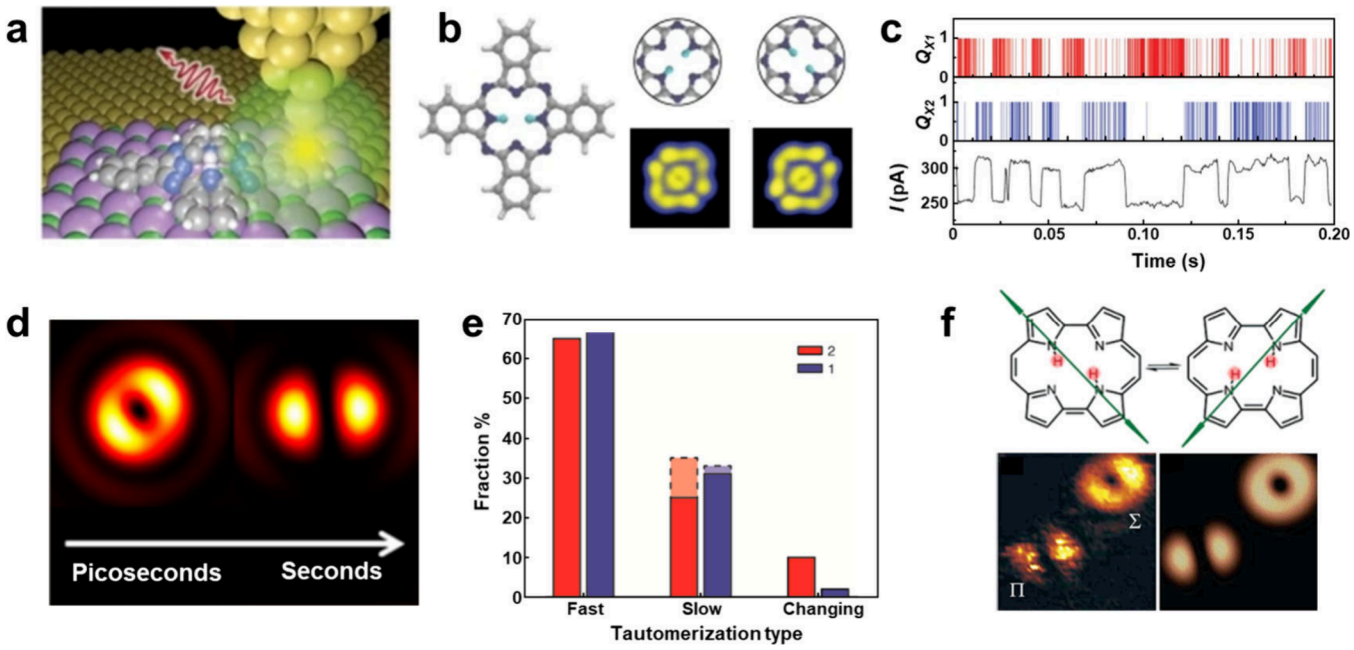

Figure 8. Single-molecule optoelectronic devices based on proton transfer. (a–c) The isomerization process of H_2Pc molecules is tracked at the single-molecule level using STM and fluorescence spectroscopy. Reproduced from ref 24. Copyright 2020 Springer Nature. (d, e) Detection of dihydrogen transfer in a single molecule by confocal fluorescence microscopy. Reproduced from ref 129. Copyright 2018 American Chemical Society. (f) Single molecule fluorescence imaging is used to directly observe isomers produced by single heavy hydrogen transfer. Reproduced from ref 116. Copyright 2005 American Chemical Society.

port properties at specific positions. Porphyrins and their derivatives are commonly used in constructing proton-transfer switching devices. In a detailed investigation, binary proton transfer in amino-functionalized porphyrin (TAPP) is studied using low-temperature STM and DFT calculations. It is found that partially deprotonated TAPP molecules undergo H-tautomerization, while fully deprotonates molecules exhibit binary stereoisomeric conformational switching[124] (Figure 7a). Liljeroth et al. demonstrated voltage-pulse-controlled removal of a single hydrogen atom from porphyrin molecules on silver, enabling a four-state switch driven by single-proton transfer.[115] Similarly, a tetraphenylporphyrin molecule on a silver surface is employed as a conductance switch. This molecule, containing two internal hydrogen atoms, can switch between two conductance states via STM current. Removal of one hydrogen atom enables a four-level switch. The device operates through single-proton transfer, representing the smallest atomic switching unit[20] (Figure 7b,c). For porphyrin molecules and their

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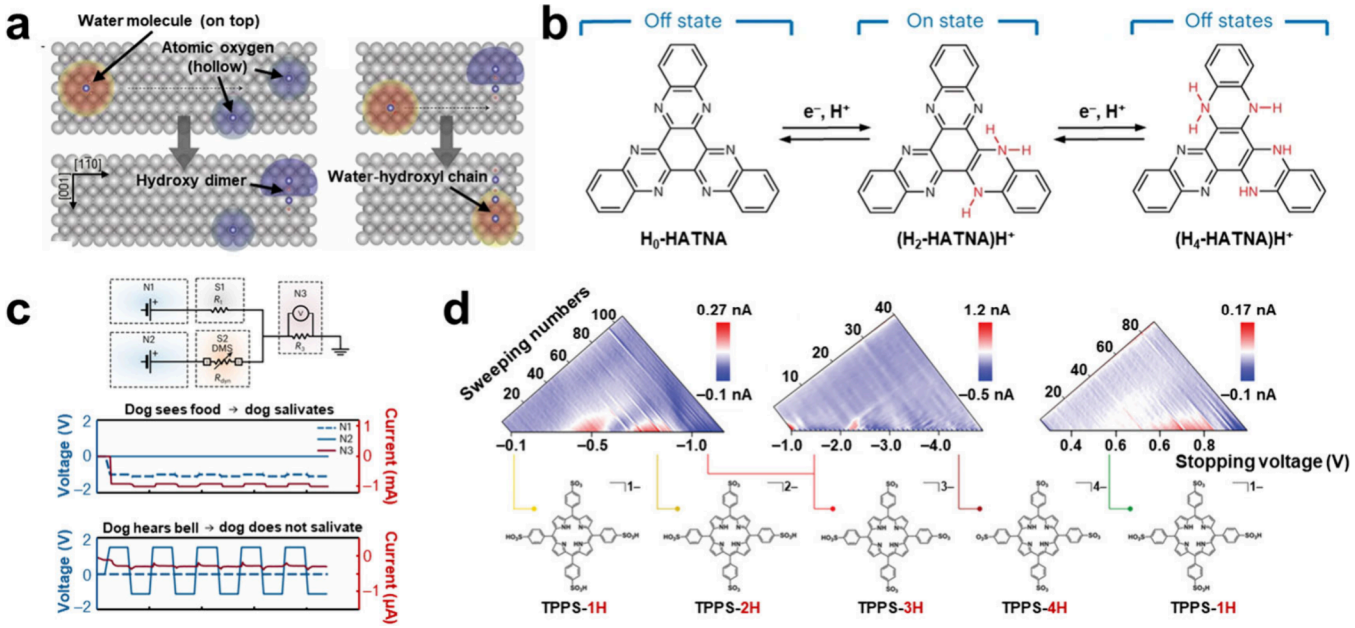

Figure 9. Other single-molecule functional devices based on proton transfer. (a) Hydrogen relay reaction at the single-molecule level. Reproduced from ref 123. Copyright 2012 Springer Nature. (b, c) DMS dependent on proton transfer for modeling biological synapses. Reproduced from ref 130. Copyright 2022 Springer Nature. (d) Fabrication of OPM using proton reservoir-type molecular TPPS for revealing proton migration and self-coordinated doping. Reproduced from ref 14. Copyright 2023 John Wiley and Sons.

derivatives, STM has proven to be an effective tool for constructing proton-transfer switches. In this context, a graphene-porphyrin-graphene single-molecule junction (SMJ) is developed with two distinct configurations: one gated by ionic liquids for high field-effect performance, achieving a maximum on/off ratio of 4800 and a gating efficiency of 179 $mV{\cdot}dec^{-1}$, and another that enables controlled proton transfer and isomerization switching without the use of ionic liquids[13] (Figure 7d). Bussetti et al. prepared two-dimensional H_2TPP layers on HOPG, which exhibit stable isomer arrangements at room temperature. Exposure to hydrochloric acid vapor reversibly converts H_2TPP to H_4TPP, enabling an acid-controlled proton transfer switch.[113]

In addition to porphyrin molecules, other types of molecules have also been used to construct proton transfer switching devices. Simpson et al. reported a metal-bonded molecular switch using substituted quinone derivatives, where hydrogen reciprocal isomerism (proton transfer) drives the switching mechanism. The $I-V$ curves show rapid current changes at a threshold voltage, indicating proton transfer activation. DFT-optimized structures and STM images provide evidence of proton transfer from amino to imino groups, elucidating the two-step process.[114] A PIPT hybrid system is developed with a pH-responsive 1,3-azulene derivative and a photoresponsive aminopyran, enabling light-driven reversible conductivity switching in single-molecule devices. Conductivity increases with light and decreases in darkness. This system successfully demonstrates the construction of single-molecule AND and OR logic gates at room temperature and pressure (Figure 7e,f).[22]

3.1.3. Single-Molecule Proton Transfer Optoelectronic Devices. In addition to switching devices, proton transfer-induced fluorescence changes in single molecules have also been observed through single-molecule devices. Doppagne et al. monitored the isomerization process of the free-base phthalocyanine (H_2Pc) molecule at the single-molecule level by combining STM and fluorescence spectroscopy. Their findings reveal that the isomerization of the H_2Pc molecule is influenced not only by changes in the atomic-scale environment but also by the involvement of its excited state in the process, which can occur even in the absence of direct electron tunneling currents through the molecule[24] (Figure 8a–c). In related work, confocal fluorescence microscopy is used to study dihydrogen transfer in porphyrin molecules within polymer matrices, revealing the impact of the environment on isomerization rates[129] (Figure 8d,e).

In addition to fluorescence spectroscopy, visualization can also be achieved through fluorescence imaging. Single-molecule fluorescence imaging is used to directly observe, for the first time, two isomers resulting from single-heavy hydrogen transfer in the porphyrinene molecule. The S_0-S_1 transition moments of the porphyrinene molecule form an angle of approximately 72° in the two isomers, aligning with the results of fluorescence anisotropy studies conducted on a large number of porphyrinenes in polymer films, thereby confirming the structural changes induced by proton transfer[116] (Figure 8f). Vasilev et al. studied free-base phthalocyanine (H_2Pc) molecules adsorbed on NaCl-covered Ag(111) surfaces at low temperatures using STM and STM-induced fluorescence measurements. The STM images illustrate the isomerization process and the evolution of the electronic structure of the H_2Pc molecules under an electric field. The relative tip-sampling distance (Δz) time trajectories and their histograms reveal how the internal charge of the H_2Pc molecule influences its fluorescence properties via the internal Stark effect.[117] The use of fluorescence spectroscopy and fluorescence imaging opens new avenues for studying proton transfer and other rapid exchange processes.

3.1.4. Other Single-Molecule Devices. In addition to single-molecule proton-transfer switching devices and single-molecule proton-transfer fluorescent devices described above, other types of proton-transfer-based single-molecule devices

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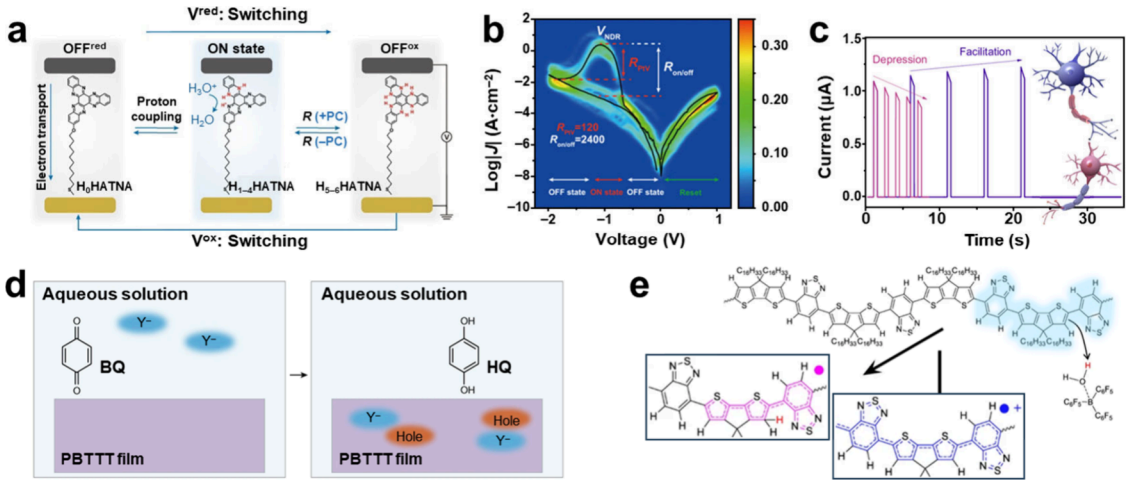

Figure 10. Working mechanism and factors of membrane devices based on proton transfer. (a, b) A molecular switch based on PCET reaction exhibits outstanding delayed NDR characteristics, and its dynamic probability is regulated by many factors. Reproduced from ref 17. Copyright 2024 Springer Nature. (c) Proton/water modulation in anthraquinone molecular junctions enables nonlinear NDR effects, dynamic hysteresis, and synaptic memory behavior. Reproduced from ref 18. Copyright 2023 National Academy of Sciences. (d) The initial and final states of p-type doping process based on PCET. Reproduced from ref 109. Copyright 2023 Springer Nature. (e) In the p-type doping mechanism of BCF, the neutral segment transfers an electron to the positively charged segment, producing a neutral protonated radical and a positively charged radical. Reproduced from ref 133. Copyright 2019 Springer Nature.

also play crucial roles. These devices enable precise control of electron and proton behaviors at the molecular level, opening up new research directions in nanotechnology and molecular electronics, and providing the potential for constructing highly integrated and functionalized molecular electronic circuits. One such mechanism is the hydrogen atom relay, which facilitates proton transfer in electrocatalytic hydrogen precipitation reactions by enhancing the rate of electrochemical hydrogen reactions at nonhomogeneous interfaces. This enables efficient hydrogen generation at low overpotentials. Kumagai et al. observed and manipulated the hydrogen atom relay reaction on the surface of Cu(110) in real time using STM at the single-molecule level, demonstrating controlled and reversible transfer. The hydrogen atom transfer is initiated by molecular vibrations excited through inelastic tunneling electrons, a process that is not only controllable but also directly monitorable via the current signal of the STM[123] (Figure 9a). Besides, proton-modulated molecular neuromorphic devices, which utilize proton modulation to mimic synaptic signaling, represent a new type of computational device. These devices show great potential in fields such as pattern recognition and artificial intelligence, as they rely on the movement of protons in an electrolyte layer. A dynamic molecular switch (DMS) based on a PCET process was developed, enabling a molecule to switch between different oxidation and protonation states, resulting in significant changes in electrical conductivity. Ambient humidity, acting as a proton source, plays a crucial role in the performance of the DMS, as a lack of protons under low humidity conditions prevents the switch from exhibiting negative differential resistance (NDR) effects. Through proton transfer, the DMS is capable of mimicking the dynamic behavior and plasticity of biological synapses, exhibiting learning and memory properties similar to those of biological neurons[130] (Figure 9b,c). To achieve ultralow-power and nonvolatile synaptic weight regulation, a proton reservoir-type molecule, 4,4′,4″,4‴-(porphine-5,10,15,20-tetrayl)tetrakis(benzenesulfonic acid) (TPPS), was designed and fabricated. Based on this molecule, an organic proton membrane memory (OPM) was developed. The proton migration and self-coordinated doping processes were revealed by observing the current changes induced by proton migration in the TPPS molecule under different voltage scans[14] (Figure 9d).

With the development of molecular neuromorphic devices based on plasmonic modulation, the integration of organic synaptic devices has become feasible. Liu et al. further advanced this field by utilizing an ultrasmall organic synapse based on the semicrystalline polymer $PBFCL_{10}$, achieving the smallest size of 50 nm and the highest integration scale of 1 Kb to date. This is accomplished by precisely modulating plasmonic transfer and conductive nanofilament formation within the organic synaptic device. The $PBFCL_{10}$ synapse is able to switch linearly between 32 conductive states, demonstrating up to 98.89% cycle-to-cycle coherence and 99.71% device-to-device coherence-the best performance among organic devices.[131] Molecular neuromorphic devices based on proton modulation can also be constructed using peptide membranes. Peptide membranes, such as Tyr−Tyr−Ala−Cys−la−Tyr−Tyr (YYACAYY, Y7C), have been reported to exhibit proton-mediated resistive switching properties, where silver ions within the peptide membranes are reduced and migrate to form a conductive channel under voltage bias. This process involves the coupled behavior of protons and electrons. Furthermore, the proton conductivity of the Y7C peptide membrane increases with relative humidity, reaching 1.76×10^{-2} S·cm^{-1} at 90% relative humidity, indicating that proton conduction in the peptide membrane is highly sensitive to ambient humidity. Given the proton-mediated resistive switching properties of the Y7C peptide membrane and its sensitivity to ambient humidity, it was applied in the construction of artificial synapses. In this system, the accumulation and depletion of protons at the Y7C membrane/In−Ga−Zn−O (IGZO) interface under high relative humidity lead to the formation of an electrically driven double layer (EDL), which activates synaptic plasticity.[132]

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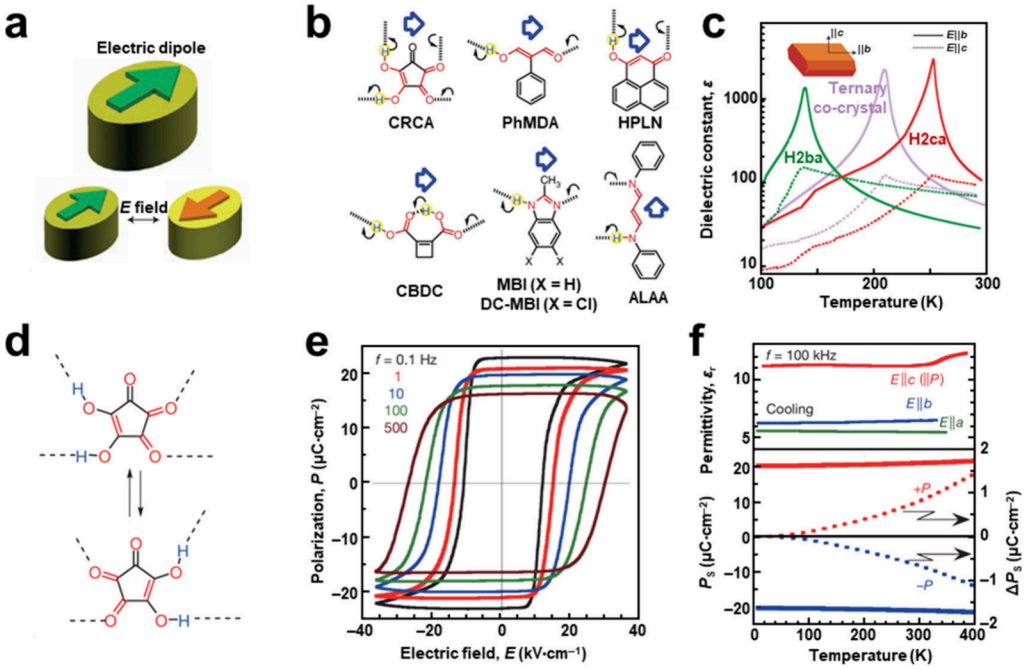

Figure 11. Ferroelectric devices based on proton transfer. (a) Bistable electron dipoles of ferroelectrics. Reproduced from ref 110. Copyright 2015 Springer Nature. (b) The crystal polarity inverted by proton transfer over a hydrogen bond and simultaneous interconversion of the single and double bonds. Reproduced from ref 134. Copyright 2017 Springer Nature. (c) The temperature dependence of dielectric constant ε measured with alternating electric field applied along the b axis and c axis of the cocrystals. Reproduced from ref 111. Copyright 2005 Springer Nature. (d) Chemical-structure polarity change through π-bond switching and proton transfer. (e) Electric polarization hysteresis with an alternating electric field E of various frequencies f. (f) Temperature dependence of relative permittivity ε_r and spontaneous polarization P_s from pyroelectric current measurements. Reproduced from ref 120. Copyright 2010 Springer Nature.

3.2. Molecular Film Devices

3.2.1. Proton Transfer in Membrane Devices. In the field of molecular electronics, proton transfer processes within molecular films have attracted considerable attention due to their high reversibility. Proton transfer, a critical phenomenon that significantly influences molecular electronic properties and transport characteristics, induces various notable effects, such as changes in dipole moment, NDR doping effects, and steric electronic interactions. These effects are crucial not only for understanding the electronic behavior at the molecular level but also for providing both theoretical insights and experimental guidance in the development of novel molecular devices. NDR is one of the significant phenomena induced by proton transfer, playing a crucial role in the design of molecular switches. Under specific conditions, the NDR effect allows the current to decrease with increasing voltage, providing a foundation for the development of efficient molecular switches. For example, a molecular switch based on PCET reactions has been proposed, exhibiting prominent hysteretic NDR characteristics with a peak-to-valley ratio of 120 ± 6.6 and a memory on/off ratio of (2.4 ± 0.6) × 10.[3] Additionally, the dynamic probability of this switch can be modulated by various factors, including bias scan rate, pH, and relative humidity. Kinetic isotope effect measurements further validate this modulation mechanism[17] (Figure 10a,b).

The nonsteady-state charge transport induced by proton transfer plays a crucial role in the study of dynamic molecular devices, involving time-dependent and history-dependent performance characteristics. Through the investigation of proton/water modulation in anthraquinone molecular junctions, Wang et al. demonstrated the potential for realizing nonlinear NDR effects, dynamic hysteresis, and synaptic memory behavior. By employing dynamic PCET kinetics, they propose a universal dynamic operation mode, offering new insights into the time-response characteristics of molecular devices[18] (Figure 10c).

Proton activity has garnered significant attention in molecular-level doping, particularly in the context of chemical doping based on PCET reactions. Ishii et al. explored the precise control of the Fermi level in organic semiconductor films at room temperature, achieved through the synergistic effect of PCET and ion intercalation. They also proposed a resistance-type pH sensor that operates without the need for a reference electrode. This study highlights the potential of proton transfer in semiconductor modulation[109] (Figure 10d). Furthermore, the doping performance of $B(C_6F_5)_3$ in solution processing is investigated, revealing that trace amounts of water significantly enhanced the doping ability of the Lewis acid by forming a Brønsted-Lewis acid complex. This discovery provides new insights into proton acid doping and lays the foundation for the optimization of future molecular doping strategies[133] (Figure 10e).

By precisely controlling the proton transfer process within molecular films, it is possible to design molecular devices with tailored electronic properties and transport characteristics. In-depth studies of these effects provide new directions for future molecular electronics and materials science, particularly in the development of molecular switches, dynamic memory devices, and efficient sensors. The multifunctionality and tunability of proton transfer processes are poised to become central to the design of novel molecular electronic devices. Research in this area not only expands the performance boundaries of molecular devices but also opens new pathways for electronics technologies based on molecular design.

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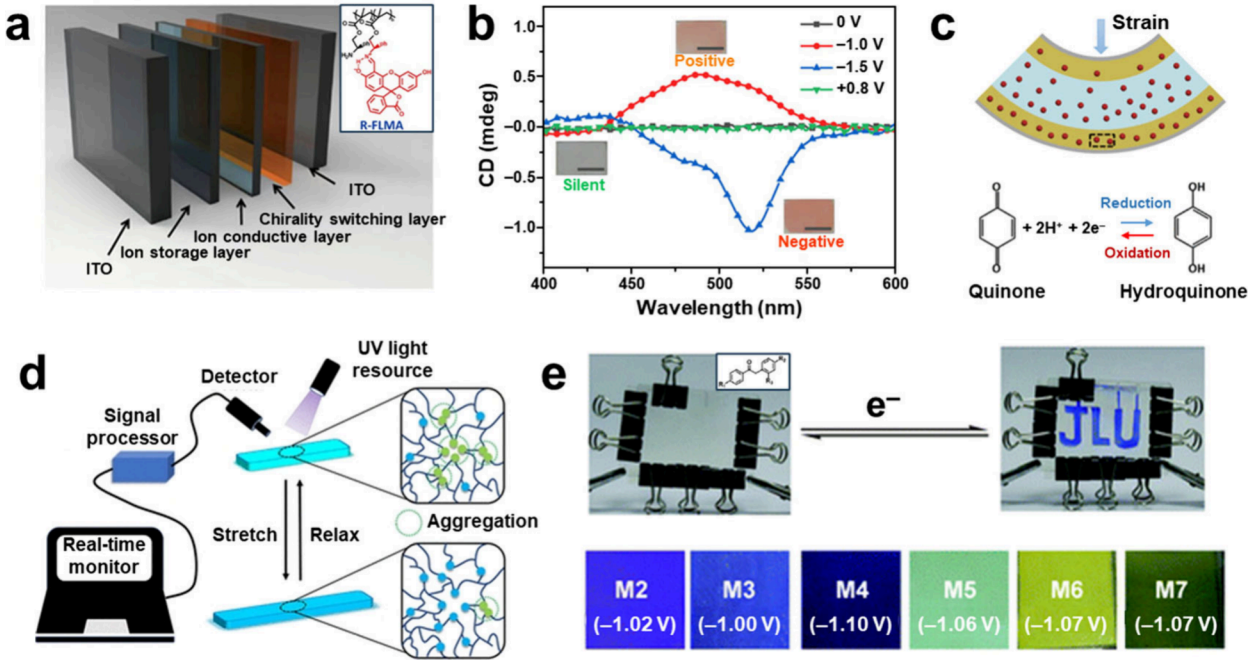

Figure 12. Switching device based on proton transfer. (a) Structure of an electric field-driven chiral switch device. (b) Reversible triple chiral switching in circular dichroism spectroscopy under voltage, along with the corresponding images. Reproduced from ref 21. Copyright 2021 John Wiley and Sons. (c) Schematic diagram of the solid-state electrochemical switches based on quinone/graphene nanomaterials. Reproduced from ref 23. Copyright 2021 American Chemical Society. (d) The force-induced chromogenic devices based on ESIPT with real-time and reversible properties Reproduced from ref 118. Copyright 2022 American Chemical Society. (e) Actual object diagram of the electro-driven display with characters and electrically switched colors in ITO devices. Reproduced from ref 135. Copyright 2013 Royal Society of Chemistry.

3.2.2. Ferroelectric Devices. Precise control of proton transfer in molecular films enables the design of devices with tailored electronic properties and transport characteristics. Studies of these effects provide new directions for molecular electronics, particularly in developing switches, dynamic memory, and sensors. The multifunctionality and tunability of proton transfer will be key in designing novel molecular electronic devices, expanding device performance and opening new avenues for electronics based on molecular design.

Ferroelectricity and supramolecular chemistry are closely linked, with order and dynamics playing a crucial role in discovering new phenomena and creating bioinspired materials that adapt to external environments. In 2015, Tayi et al. explored how supramolecular strategies have advanced organic ferroelectrics. They highlighted how noncovalent interactions can enhance ferroelectric performance, produce processable materials, and enable room-temperature operation, thanks to the structural diversity provided by self-assembly[110] (Figure 11a).

Ferroelectric devices based on proton transfer are highly influenced by temperature and electric fields, which significantly impact their performance. Ferroelectric materials utilizing proton tautomerism have been studied for operation at low fields and temperatures above room temperature. Solution-grown crystals exhibits strong pinning of ferroelectric domain walls, however, high voltage during thermal annealing and repeated bipolar pulses lead to enhanced switching performance by depinning the walls. The optimized polarization strength of these materials, comparable to or exceeding that of commercial ferroelectrics such as polyvinylidene fluoride (PVDF), demonstrates a significantly weaker coercive field by 2 orders of magnitude. Notably, the polarization strength of the keto-acid system increases from 21 to 30 $\mu C \cdot cm^{-2}$, surpassing that of some commercial materials like $SrBi_2Ta_2O_9$ and $BaTiO_3$[134] (Figure 11b).

In a further study, a strong ferroelectric response is achieved by assembling nonpolar conjugated molecules into cocrystals of low molecular weight organic compounds. The benzoxazine and chloronitrobenzoic acid cocrystals exhibit high spontaneous polarization and a dielectric constant exceeding 100 at room temperature[111] (Figure 11c).

In another investigation, ferroelectricity is demonstrated in single-component molecular crystals at room temperature. Applying an electric field to the keto-acid crystal aligned the molecular polarity, as evidenced by increased optical second harmonic generation, and produced a clear polarization hysteresis. In this pentagonal molecular system, ferroelectricity is achieved through synchronized proton transfer, rather than rigid-body rotation. These molecular crystals exhibit the highest spontaneous polarization (around 20 $\mu C \cdot cm^{-2}$) among organic ferroelectric materials, despite their small molecular size, consistent with first-principles electronic structure calculations. This work underscores the potential of proton transfer in enabling high-performance organic ferroelectrics and advances the field of molecular electronics[120] (Figure 11d–f).

3.2.3. Switching Devices. Proton transfer switch devices control state transitions by altering charge distribution through proton migration. This enables rapid, multistable state changes and precise control under electric, light, or temperature stimuli. Their dynamic properties make them ideal for molecular switches, sensors, and memory devices. By regulating proton transfer, these devices achieve reversible, low-energy, and fast switching, showing great potential in intelligent control, storage, and computation. As a result, proton transfer devices are a key research focus for novel functional technologies.

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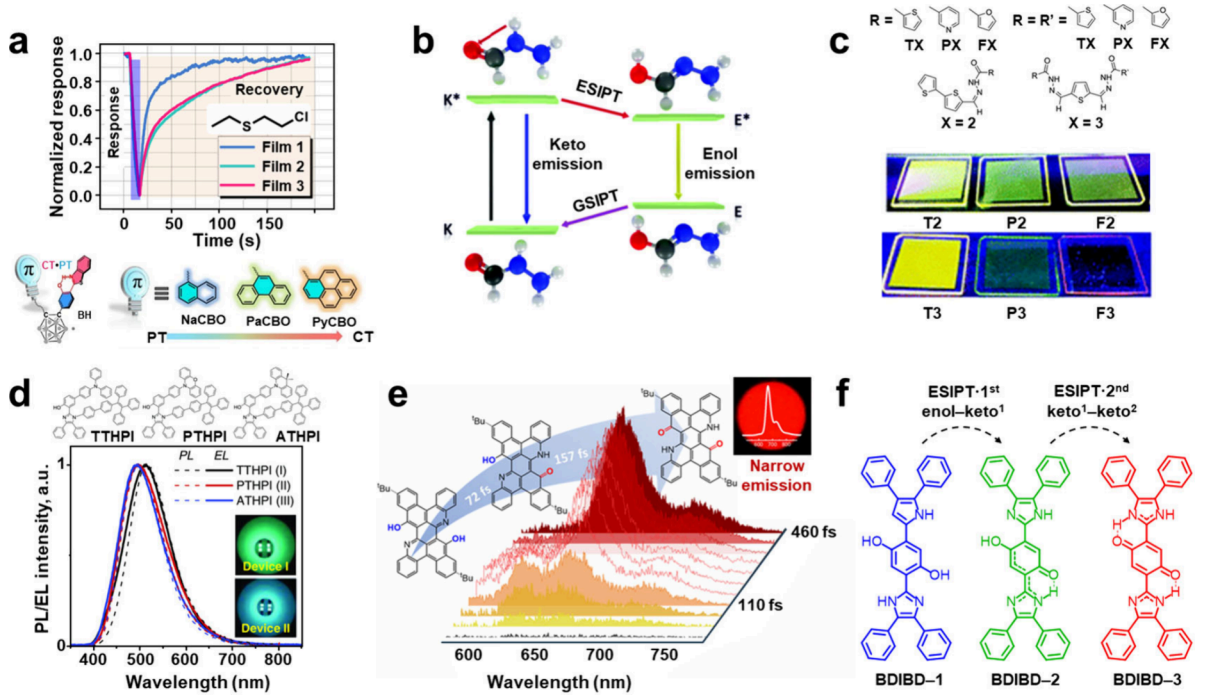

Figure 13. (a) Fluorescent responses of the sensor array and chemical structures of the fluorophores. Reproduced from ref 25. Copyright 2023 American Chemical Society. (b) The general mechanism of keto−enol tautomerism exhibited in acidic hydrazone. (c) Solvent-induced chromic phenomena in hydrazone compounds. Reproduced from ref 26. Copyright 2019 Royal Society of Chemistry. (d) The chemical structures of relevant molecules, electroluminescent and photoluminescence spectra of nondoped OLEDs, and the corresponding emissive layers. Reproduced from ref 27. Copyright 2021 John Wiley and Sons. (e) The spectral temporal evolution of DPNA-tBu. Reproduced from ref 119. Copyright 2024 American Chemical Society. (f) Organic photoluminescent molecule achieving full-color emission via enol−keto tautomer modulation. Reproduced from ref 136. Copyright 2023 American Chemical Society.

Chiral optical switches, which can alter optical properties under external stimuli, are essential for applications in chemical sensing, enantiomer recognition, molecular devices, and information storage. Research on proton transfer in molecular films has provides valuable insights for designing simple, rapid, reversible, and durable chiral molecular switches. A novel electric-field-driven multichirality switching device is developed by combining a chiral polymer switch (R-FLMA) with hydroquinone (*p*-BQ) via PCET. This device can switch between three stable chirality states (silence/negative/positive) within the visible spectrum and is reversibly controlled over 1000 cycles through voltage adjustments. The switching process also induces color and fluorescence changes, demonstrating its potential as a spatial light modulator[21] (Figure 12a,b).

To address the low sensitivity and poor cycling stability of traditional electrochemical sensors, a high-performance sensor based on PCET is developed. This PCET mechanism, first reported in sensors, is validated using ultraviolet−visible spectroscopy (UV−Vis) spectroscopy. It relies on the reversible reaction between hydrogen ions and quinone molecules, significantly enhancing both sensitivity and cycling stability. This ultrasensitive sensor can detect a wide range of human activities, from large movements to subtle physiological signals, enabling complex functions such as Braille and handwriting recognition[23] (Figure 12c).

In the field of pressure-sensitive color change, real-time monitoring of strain/stress in polymers remains a significant challenge. To address this, Hu et al. developed a novel force-induced chromophore, PhMz-4OH, based on ESIPT, which exhibits real-time and reversible force-induced color change characteristics when incorporated into polyurethane. The ketone emission of PhMz-4OH is observed only in the TCM/DMF mixed solution and in the solid state, indicating that the ESIPT of PhMz-4OH is active in the aggregated state. Subsequently, PhMz-4OH is incorporated into polyurethane (PhMz-4OH@PU). The PhMz-4OH@PU composites with varying concentrations exhibits concentration-dependent emission, attributed to the aggregation of PhMz-4OH. Control experiments with PhMz-2OH@PU and PhMz-NH_2@PU confirm that the fluorescence color change is indeed induced by force transmitted through the polymer chains, and theoretical calculations are consistent with the experimental observations. This study may pave the way for advancements in real-time stress/strain sensing in polymers[118] (Figure 12d).

In a related study, methyl ketones are designed as switching units for molecular color switches controlled by electric addresses. Cyclic voltammetry (CV), X−ray photoelectron spectroscopy (XPS), infrared spectroscopy (IR), and in situ UV−Vis clearly demonstrate a novel "electro-acid−base" (radical ion) induced intermolecular proton transfer color-switching mechanism. Significant spectral absorption shifts of approximately 291 nm are observed during the switching process. By adjusting the substituents on the methyl ketone bridging unit, blue, yellow, and green colors are achieved. The in situ "electro-acid−base" mechanism is more convenient than traditional chemical stimuli (acid or base) for regulating molecular switching characteristics[135] (Figure 12e).

3.2.4. Photoelectric Devices. Proton migration within a material can significantly alter the electronic structure and charge distribution, enabling rapid adjustment of optoelectronic properties under external stimuli. This offers a flexible

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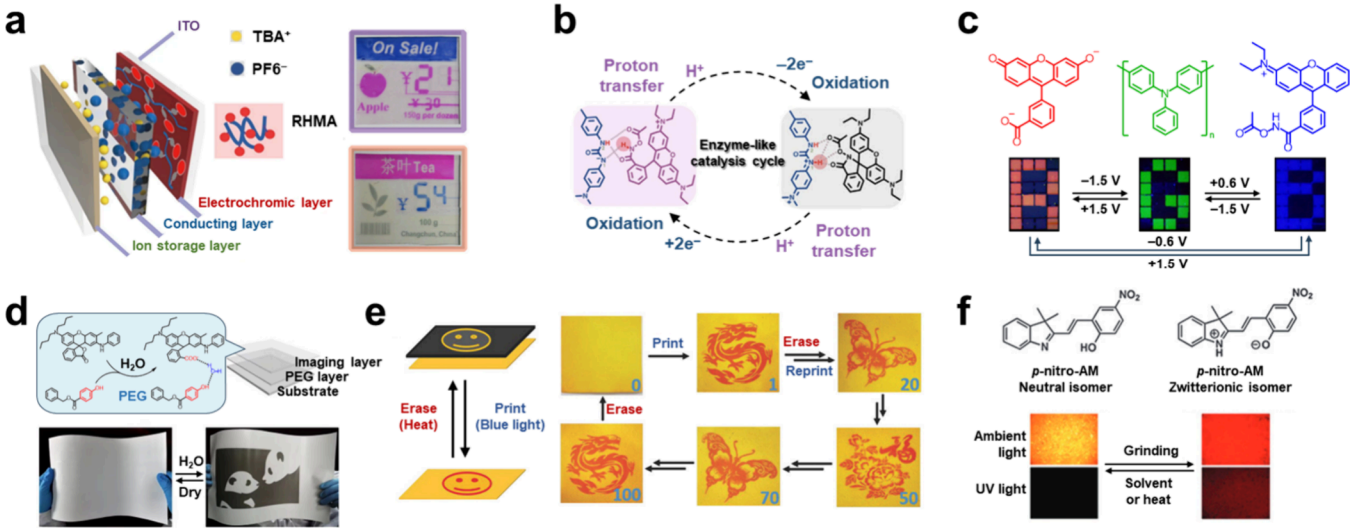

Figure 14. Multifunctional response devices based on proton transfer. (a) Schematic of an electrochromic device. Reproduced from ref 28. Copyright 2019 Springer Nature. (b) Proposed mechanism of the electrochromic system. Reproduced from ref 121. Copyright 2019 Springer Nature. (c) Single-pixel RGB electrofluorescent color-changing devices with red, green, and blue fluorescence. Reproduced from ref 138. Copyright 2020 John Wiley and Sons. (d) Preliminary structure and hydrochromic system composition of water-jet rewritable paper in the imaging layer, along with the paper before and after water printing. Reproduced from ref 122. Copyright 2018 Springer Nature. (e) Application of binary photochromic materials, combining PAHs with acid-responsive dyes in the paper. Reproduced from ref 15. Copyright 2018 John Wiley and Sons. (f) The color-changing sensing display of proton transfer/exchange systems induced by stress stimuli. Reproduced from ref 139. Copyright 2013 Royal Society of Chemistry.

approach to regulating optoelectronic devices. Proton transfer enhances conventional materials and provides new insights for designing photodetectors, photosensitive devices, and solar cells. For example, electronic structural changes from processes like ESIPT lead to distinct electroluminescent characteristics before and after proton transfer, making these molecules ideal for OLED applications.

ESIPT is a photophysical process of great interest in metal−organic supramolecular optical materials. ESIPT materials exhibit a unique four-level cycle with multiple emission peaks originating from the alcohol and ketone forms, leading to tunable luminescent properties. Recent advancements in understanding these materials have been propelled by techniques such as in situ X−ray diffraction and transient photophysical studies. ESIPT enables dual fluorescence emission and is utilized in organic light-emitting diodes to achieve the high-performance electroluminescence. A notable contribution in this area is made by Liu et al., who introduced a strategy to regulate ESIPT by combining it with excited-state intramolecular charge transfer (ESICT). They design three carbon-borane derivatives—NaCBO, PaCBO, and PyCBO—in which 2-(2′-hydroxyphenyl)-benzothiazole acts as the ESIPT unit (electron acceptor), while naphthyl (Na), phenanthryl (Pa), and pyrenyl (Py) serve as electron donors. The molecules' face-to-face arrangement enables continuous modulation of the ESIPT/ESICT processes through donor ability and solvent polarity, resulting in distinct emissions. These molecules also feature porous structures and exhibit varied fluorescence colors, enabling the selective detection of the mustard gas simulant, 2-chloroethyl ethyl sulfide, with a 50-ppb detection limit and a response time of just 5 s. This work presents a reliable strategy for the development of high-performance fluorescent probes through the regulation of ESIPT[25] (Figure 13a).

Hydrazone compounds, well-known for their application in OLEDs, provide an excellent platform for exploring proton transfer in photophysical processes. For example, TX, PX, and FX (X = 2, 3) molecules, which incorporate hydrazone groups, demonstrate attractive ESIPT. These molecules, when used in OLED devices, exhibit electroluminescence. Theoretical analysis reveals that TX, PX, and FX possess extended conjugation, which enhances the efficiency of ESIPT compared to the X = 1 variant. Solvent-induced chromic studies show dual emission peaks in THF, a characteristic feature of ESIPT, with some molecules also exhibiting dual peaks in the solid state. However, aggregation-induced emission is not observed. Energy scans indicate lower forward barriers in the excited state, facilitating ESIPT, while potential energy surface scans suggest that double proton transfer is not feasible, and stepwise double proton transfer presents significant challenges[26] (Figure 13b,c).

In another study, Kumsampao et al. developed a series of solid-state fluorophores (TTHPI, PTHPI, and ATHPI) that exhibit both ESIPT and AIE properties.[27] These molecules are designed with 2-(2-hydroxyphenyl)-1,4,5-triphenylimidazole as the ESIPT core, combined with AIE-active fluorophores such as tetraphenylethene and hole-transporting groups (e.g., triphenylamine). The combination of AIE and efficient hole transport enhances solid-state emission. Both theoretical and experimental studies confirm that all three fluorophores demonstrate ESIPT and AIE characteristics, emitting strong cyan/green light with photoluminescence quantum yields ranging from 41% to 74%. These fluorophores also exhibit high thermal and electrochemical stability, good hole mobility, and are successfully applied in OLEDs. The TTHPI-based device, in particular, achieves excellent electroluminescence performance, with a maximum external quantum efficiency of 5.21% and a current efficiency of 11.17 cd·A^{-1} (Figure 13d).[27]

Dihydrogen-bonded emitters have been studied for their strong, narrow-band red electroluminescence in OLEDs, attributed to enol−keto isomerization and excited-state proton transfer. Absorption and emission analyses reveal ground-state

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isomerization between enol−enol (EE), enol−keto (EK), and keto−keto (KK) isomers, with multiple proton transfers occurring in the excited state. The tightly packed π-conjugation in the KK state produces strong red emission, while its small rearrangement energy enhances the vibrational peak, narrowing the emission's full width at half-maximum (fwhm) to 39−40 nm. OLEDs utilizing sensitization methods demonstrate deep red emission at 660 nm with high external quantum efficiency, offering a promising strategy for the development of deep red and near-infrared ESIPT molecules[119] (Figure 13e).

Yi et al. developed a novel design for organic photoluminescent molecules with dual ESIPT sites. This emitter enables tunable emission through enol−ketone (1st) to ketone (2nd) isomeric transitions, achieving full-color emission from blue to red, including white light, in different solvents. Transient photophysical studies revealed a precursor (<0.8 ps)-relay absorption relationship between the ketone states, leading to dual emission on the nanosecond time scale (∼1900 ps). Theoretical analysis confirmed a low-energy barrier for the double proton transfer, supporting experimental results. This system, based on intramolecular double proton relay transfer, expands optical responses and enables full-color display, providing a reference for advanced dual-ESIPT optical materials[136] (Figure 13f).

3.2.5. Multifunction Response Devices. Proton transfer alters molecular properties, impacting device transport and optoelectronic responses, and leads to unique optical properties. External stimuli such as electric fields, temperature, light, or chemical reactions can induce adjustable changes in device color, brightness, transparency, and performance. This color-changing effect is crucial in modern materials science. Color-changing devices exhibit high reversibility, fast response, and precise tuning under varying conditions, with potential applications in smart displays, optical control, sensing, temperature regulation, and inkless printing. These devices represent a significant direction for designing multifunctional smart materials and devices. Electrochromism, controlled by an electric field, alters molecular geometry or electronic structure via proton transfer, causing reversible color changes. This method offers rapid response, low energy consumption, and high stability, with potential applications in smart displays, information storage, and optoelectronic control.[137]

Concretely, a bistable electrochromic device based on intramolecular PCET has been designed, achieving excellent overall performance. The device demonstrates dual stability (>52 h), reversibility (>12,000 cycles), coloration efficiency ($\geq$1,240 $cm^2 \cdot C^{1-}$), a transmittance change of 70%, and rapid switching ($\leq$1.5 s). The design principles derived from this unconventional synergistic intramolecular PCET exploration may also prove useful in various optoelectronic applications[28] (Figure 14a).

Reversible electro-acid/electro-base systems in electrochromic materials can be divided into two types: bistable electrochromic materials and electrofluorescent color-changing materials. In bistable systems, 1-(4-(dimethylamino)phenyl)-3-(p-tolyl)urea (Urea-N) acts as the electro-acid, and 3′,6′-bis(diethylamino)-3-oxospiro[isoindoline-1,9′-xanthen]-2yl-acetate (Rh-M) as the color-switching molecule. Color changes occur through proton transfer between them. Oxidation of Urea-N leads to magenta Rh-M, while reversing the voltage returns Rh-M to its original colorless state[121] (Figure 14b). In electrofluorescent systems, RGB devices emit blue, red, and green fluorescence in neutral, positive, and negative voltage states, respectively. Color interference is avoided by quenching blue fluorescence under other voltage conditions[138] (Figure 14c).

Recent advancements in color-changing devices, including chemical, thermochromic, photochromic, and mechanochromic systems, have gained significant attention, particularly by incorporating proton-transfer mechanisms. These studies leverage proton-transfer-induced changes in molecular structure and electronic states to modulate optical properties. External stimuli like thermal, optical, or mechanical stress trigger unique dynamic responses, providing a strong foundation for designing multifunctional color-changing devices.

Drawing inspiration from thermochromic binary systems and biochemical reactions involving proton transfer through water networks, a water-induced color-changing system is developed using benzyl 4-hydroxybenzoate (B4H) as a proton donor and 2-phenylamine-6-di-*n*-butylamino-3-methylfluorene (ODB-2) as the chromophore, with polyethylene glycol (PEG) as an additive. In this system, ODB-2 undergoes isomerization via proton transfer from B4H, with PEG stabilizing the process. Water functions as a proton transfer bridge and ion stabilizer, enabling the dye to undergo color switching. PEG also contributes to creating rewritable paper and stabilizing the initial colorless form of ODB-2[122] (Figure 14d).

Polycyclic aromatic hydrocarbons (PAHs) that release and recapture protons under light and dark conditions have been studied, creating a binary photochromic system with acid-responsive dyes. They investigated the use of these materials in light-responsive rewritable paper (LRP) using pH-sensitive dyes. In darkness, a PAH-MO mixture is yellow, with PAH in its open-ring state and methyl orange (MO) nonprotonated. Blue light irradiation causes PAH to transition to its colorless closed-ring form, releasing protons to MO and turning the solution orange. A new prototype of visible-light responsive rewritable paper (VLRP) was developed, incorporating fiber, PEG, MO, and PAH layers, with PEG providing a stable microenvironment for proton transfer[15] (Figure 14e).

Proton transfer induced by pressure or stress stimuli and its application in mechanochromism have been widely explored to investigate molecular/submolecular proton transfer under external stress. Wang et al. synthesized four twisted molecules with different substituents and hydrogen bonding to study proton transfer under stress. 2-(2-(3,3-Dimethyl-3H-indol-2-yl)ethenyl)-4-nitrophenol (*p*-nitro-AM) changes color from yellow to red upon grinding, while 2-(2-(3,3-dimethyl-3H-indol-2-yl)ethenyl)phenol (AM), 2-(2-(3,3-dimethyl-3H-indol-2-yl)ethenyl)-6-nitrophenol (*o*-nitro-AM), and 2-(2-(3,3-dimethyl-3H-indol-1-ium-2-yl)ethenyl)-4,6-dinitrophenol salt (dinitro-AM) do not. The color change in *p*-nitro-AM can be reversed by solvent treatment or thermal processing, suggesting that the solvent facilitated reverse proton transfer[139] (Figure 14f).

3.3. COF- and MOF-Based Devices

Hydrogen transfer, especially proton transfer, plays a key role in the stability and reactivity of COFs and MOFs. Proton transfer not only regulates the electronic structure and geometric configuration of molecules but also affects the charge transport and chemical stability. By introducing proton transfer mechanisms, materials can adaptively respond to different environmental conditions, enhancing their stability and reactivity. In addition, in molecular electronics, proton

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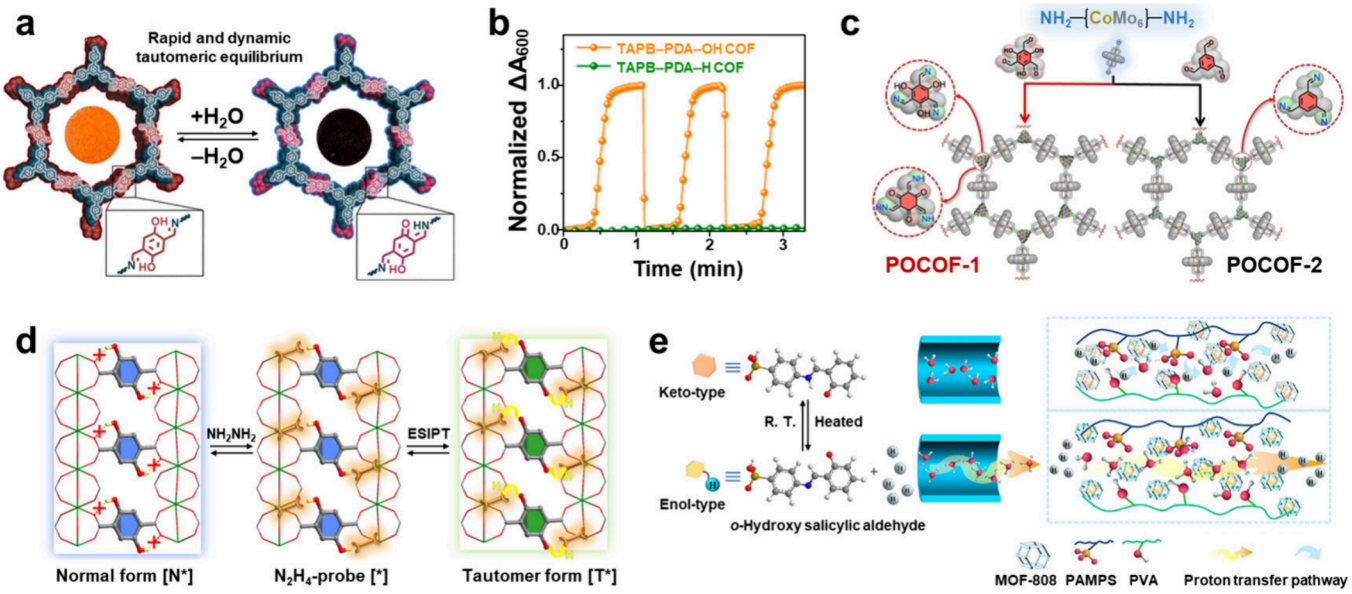

Figure 15. COF and MOF material devices based on proton transfer. (a) COFs showing a new visible absorption band in the presence of water. (b) Humidity sensing COF films with absorbance changes. Reproduced from ref 29. Copyright 2020 American Chemical Society. (c) Synthetic pathway and structure of POCOF-1 and POCOF-2. Reproduced from ref 112. Copyright 2023 John Wiley and Sons. (d) Sensing mechanism of MOFs enabling selective analyte recognition via hydrogen bonding, with analyte-assisted ESIPT and ratiometric emission for ultrafast signal transduction. Reproduced from ref 140. Copyright 2021 American Chemical Society. (e) Proton conduction mechanism of host−guest MOF composite. Reproduced from ref 141. Copyright 2023 American Chemical Society.

transfer within COFs and MOFs has gained significant attention. The 3D ordered architectures of COFs and MOFs facilitate proton transfer across larger scales and more intricate geometries, compared to 2D molecular membranes. By tuning their structure, porosity, and transport properties, COFs demonstrate behaviors such as charge localization, electron transfer, thermal responsiveness, and ionic conductivity. These characteristics provide insights into proton transfer mechanisms in 3D porous materials and pave the way for developing COF-based devices for energy storage, sensing, catalysis, and advanced functional systems. For example, Jhulki et al. have reported a COF with a 2,5-bis(imine)-substituted 1,4-dihydroxybenzene motif that undergoes rapid, reversible color changes in polar solvents due to diimine and imine/cis-ketoamine isomerization. The COF-based humidity sensor shows fast response, stability for months, and distinct absorption in humid environments[29] (Figure 15a). A polyoxometalate COF (POCOF) is developed using a solvothermal strategy, introducing keto−enol isomerism for the first time in COFs. This innovation improves the chemical stability and electrochemical performance of the material, achieving an energy density of 56.2 $Wh{\cdot}kg^{-1}$. These advancements underscore the potential of isomerism in the design of high-performance sensors and energy storage electrodes[112] (Figure 15b).

Proton transfer in COFs and MOFs, with their ordered structures, tunable pore sizes, and chemical stability, provides an ideal platform for efficient proton conduction. Jia et al. have developed a hydrazine (N_2H_4) sensor using an indium-dihydroxyterephthalic acid MOF (SNNU-153). The framework achieves selective recognition through analyte-MOF hydrogen bonding and an ESIPT process, with ratiometric fluorescence emission as the signaling mechanism. SNNU-153 exhibits an "on−off" fluorescence response to hydrazine, discriminating it from analogs like NH_3 and NH_2OH. The rapid response (<300 ps), wide concentration range, reproducibility, and high selectivity highlight its potential for diverse applications[140] (Figure 15c). A thermoresponsive proton-conductive MOF composite has been introduced, where proton conductivity is controlled by reversible keto−enol isomerization of HBABSA within the MOF-808 pores. The hybrid membrane, blended with PVA/PAMPS, shows an enhanced conductivity of 5.57×10^{-3} $S{\cdot}cm^{-1}$. These properties make it ideal for thermal sensors, smart batteries, and telecontrol systems. By designing metal nodes and organic ligands to introduce proton transfer pathways, MOFs are positioned as key materials for next-generation proton transfer devices. Their 3D structures can integrate proton transfer mechanisms, expanding their use in proton conduction, switching, and sensing applications, advancing proton transfer in multidimensional materials[141] (Figure 15d).

In conclusion, proton-transfer-based devices have advanced significantly in single-molecule systems, molecular films, and ordered frameworks (COFs/MOFs), enabling precise control of molecular configurations, electronic states, and charge transport. Single-molecule devices utilize proton transfer for atomic-scale switching, optoelectronics, and neuromorphic functions, while molecular films exploit proton-mediated phenomena like NDR effects and ferroelectricity for sensing and memory. COFs/MOFs extend proton dynamics to 3D architectures, enhancing conduction and stimuli-responsive sensing. Future efforts could focus on optimizing interfacial transport and engineering hybrid systems for nanoelectronics, energy-efficient computing, and biomimetic technologies, positioning proton-driven devices as key enablers in next-generation molecular electronics. Future HT integration could focus on three fronts: pathway precision, novel device architectures, and application expansion. Advanced methods combining molecular engineering, external stimuli, and computational modeling optimize HT dynamics and selectiv-

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ity, enabling next-generation molecular devices. Atomic-level simulations map energy landscapes to guide efficient systems, accelerating breakthroughs in molecular electronics, catalysis, and energy storage. These approaches could achieve sub-0.1 V operational voltages through optimized charge transport dynamics while enabling device miniaturization via suppressed Joule heating effects, therefore addressing key challenges in power efficiency and scalability for next-generation microelectronics applications and advancing the development of environmentally sustainable electronic industries.

4. CONCLUSIONS AND PERSPECTIVES

As a critical chemical process in functional molecules and molecular devices, hydrogen transfer has driven remarkable progress in fundamental research and practical applications. Despite these advances, extending practical applications of HT in molecular science remains significant challenges. Future efforts should focus on developing efficient reaction systems, optimizing device performance, and exploring emerging application areas to unlock the potential of HT for next-generation functional materials and devices.

4.1. Precise Control over HT Pathways

Complex interactions within molecules and the influence of external conditions make precise control of HT pathways and selectivity a significant challenge. Key issues include site, spatial, and chiral selectivity of HT[153] as well as controlling reaction products and catalytic efficiency, requiring advanced theoretical and experimental approaches to uncover HT reaction mechanism under complicated factors and multiple time and space scales. For theory, the development of reaction kinetics simulation programs for open systems (e.g., DFT +NEGF[154,155]) and multiscale complex system simulation methods can help people more accurately predict quantum effects and high-energy processes in HT.[81] Experimentally, high-space-time resolution techniques are essential for monitoring HT processes in real-time. high-resolution and ultrafast techniques, such as the combination of STM and femtosecond pump−probe spectroscopy, enable real-time observation of hydrogen transfer at the single-molecule scale.[24,108] For instance, fluorescence-STM coupling has demonstrated the capability to track proton transfer dynamics in real time.[24] However, quantitative characterization of hydrogen transfer kinetics still faces limitations: indirect Arrhenius-based barrier estimation methods introduce uncertainties of ±0.1 eV,[11,124] even with recent advances achieving millisecond temporal resolution in kinetic measurements.[127] Tailored molecular designs, focusing on bond lengths, electronic density, and hydrogen-bond networks, can further refine HT efficiency and selectivity,[21,23,82,118] paving the way for multifunctional molecular devices. In practical applications, external stimuli such as light, electric fields, or magnetic fields offer promising avenues for pathway control.[13,24,111] Light-induced ESIPT and PIPT mechanisms can enable precise regulation in photoresponsive devices,[26,27,119] enabling advanced designs like light-controlled molecular logic gates.

4.2. Expanding Device Designs

While proton transfer in molecular devices has been extensively explored, the potential of HAT and hydride transfer remains underexplored. These processes involve more intricate electronic coupling and orbital reconstruction than proton transfer, offering unique advantages for high-performance devices. HAT mechanisms enable the development of molecular switches and sensors. For example, by designing hydrogen-sensitive molecules, HAT can be triggered in molecular devices in response to specific light wavelengths or other field changes, facilitating photoresponsive or force-sensitive switching.[156,157] In addition, radical-mediated HAT reactions offer opportunities to dynamically modulate molecular magnetic and conductive properties.[142,143] This capability is highly relevant for quantum computing and spintronics. Hydride transfer plays a significant role in energy conversion devices such as fuel cells, batteries, and catalytic systems. Molecular devices that can mimic enzymatic hydride transfer[158] could be used in catalysis and energy applications to enable selective hydrogenation reactions and energy production. Hydride transfer can also significantly alter molecular electronic structures, making it a promising candidate for highly efficient charge transfer in molecular switches and circuits.[144,145] To enhance the practical application of these devices, improving device stability, responsiveness, integration, and scalability is crucial.[82] Strategies such as encapsulation within protective frameworks and supramolecular cages, as well as interfacial protection on 2D materials, can help achieve this. Embedding HT-active molecules in hybrid materials such as MOFs[106] or 2D materials can enhance environmental robustness, while multifield coupling methods can boost the responsiveness[34,35,59] for applications in bioimaging and sensing.

4.3. Exploring Emerging Applications

HT-based molecular devices are expected to make significant advancements in various emerging fields due to their versatility and responsiveness to external stimuli such as light, pH, strain, and electric fields. In electronics, HT mechanisms enable molecular-scale logic operations, paving the way for low-power, highly integrated memory and computing devices. This could also transform flexible electronics, wearables, and smart sensors. However, challenges remain in ensuring stability and scalability, which require optimized molecular designs. In catalysis, HT-based devices[101] show promise in advancing clean energy technologies such as fuel cells and water splitting. By improving hydrogen atom and hydride transfer pathways, they can enhance reaction efficiency and selectivity. In biology, HT processes enable bioimaging, molecular sensors, and targeted drug delivery,[159−161] while challenges in precisely regulating HT dynamics within biological systems drive innovations in high-sensitivity sensors and advanced imaging for transformative biomedical breakthroughs.

In conclusion, hydrogen transfer is a key mechanism in functional molecules and devices, offering significant potential for both fundamental research and practical applications.[146−152] This review highlights the mechanisms, key processes, and diverse applications of HT. With ongoing advances in mechanism understanding and regulation, HT-based devices are expected to drive breakthroughs in smart materials, information technologies, and energy solutions.

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Notes

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