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The Host-Guest Assemblies of Metal–Organic Frameworks and Protic Ionic Liquids With ZIF-8 and [Dema][TfO] – Structural Response and Ionic Conductivity

Wen Yang^{1,2}  | Christian Rodenbücher¹  | Sylvio Indris³  | Benjamin Klingebiel⁴  | Mareen Schaller³  | Nan Sun⁴  | Jiangshui Luo⁵  | Carsten Korte¹ 

¹Institute of Energy Technologies (IET-4), Forschungszentrum Jülich GmbH, Jülich, Germany | ²Faculty of Mathematics, Computer Science and Natural Sciences, RWTH Aachen University, Aachen, Germany | ³Institute For Applied Materials-Energy Storage Systems (IAM-ESS), Karlsruhe Institute of Technology (KIT), Karlsruhe, Germany | ⁴Institute of Energy Materials and Devices (IMD-3), Forschungszentrum Jülich GmbH, Jülich, Germany | ⁵College of Materials Science and Engineering, Sichuan University, Chengdu, People's Republic of China

Correspondence: Jiangshui Luo (jiangshui.luo@scu.edu.cn) | Carsten Korte (c.korte@fz-juelich.de)

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ABSTRACT

The synergy between ionic liquids (ILs) and metal–organic frameworks (MOFs) has attracted considerable attention because of future applications as a tailor-made hybrid ionic conductor. The incorporation of ILs into MOFs cages has led to the development of a novel type of solid electrolytes (ILs@MOF), characterized by exceptional thermal stability and high conductivity for large ionic species. In this study, an efficient capillary method was employed to introduce a classical protic IL, [Dema][TfO], into ZIF-8 pores, consisting of sodalite-type cages ($\text{Zn}(\text{MeIm})_2$). Our investigation focuses on the influence of varying ILs content on the free (pore) volume, thermal stability, microstructure, and ionic conductivity. The uptake of [Dema][TfO] results in a ZIF-8 cage expansion, accompanied by a decrease of the decomposition temperature. Upon infiltration of [Dema][TfO] into the ZIF-8 pores, the preexisting hydrogen bonds within the IL are broken due to confinement effects. Notably, when ZIF-8 pores are entirely saturated with [Dema][TfO], the composite material exhibits an ionic conductivity of $1.09(6) \text{ mS}\cdot\text{cm}^{-1}$ (at 160°C under anhydrous conditions) with an activation energy of $0.45(3) \text{ eV}$, which is better than other ILs@MOF conductive composites. These findings reveal ILs@MOF hybrid composites are versatile systems to compose protic conductors, attributable to their elevated ionic conductivity.

1 | Introduction

Proton conduction is a fundamental phenomenon, bearing significance not only in natural ecosystems but also in solid materials, playing a pivotal role in crucial energy technologies like fuel cells [1–3]. While traditional perfluorinated polymers grafted with sulfonic acid moieties such as NAFION have conventionally served as proton conductors, a growing interest has emerged in

exploring innovative avenues. Among these, crystalline solids, covalent organic frameworks, hydrogen-bonded organic frameworks, as well as MOFs, stand out as promising candidates with potential as novel proton conductors [4, 5]. MOFs and coordination polymers, in particular, have garnered substantial attention due to their dynamic evolution as crystalline materials, offering structural versatility and precise controllability [6]. Their intricate hydrogen-bonding networks and water clusters further

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augment their capacity for swift and efficient proton exchange [7]. Consequently, considerable efforts are underway to attain heightened proton conductivity properties of MOFs.

ILs have emerged as highly promising candidates for serving as exceptional electrolytes in electrical energy storage devices [8, 9]. These environmentally friendly solvents exhibit a host of remarkable characteristics, including negligible volatility, non-flammability, exceptional thermal and electrochemical stability, and an impressive ionic conductivity [10]. Nevertheless, akin to organic solvents, the liquid state of ILs can potentially result in leakage and subsequent equipment corrosion. MOFs have garnered extensive scientific and technological interest due to their tunable pore size, adaptable geometric configurations, and structurally designable nature [11]. This inherent property of MOFs renders them particularly promising for the development of novel solid ionic conductors by incorporating conductive ILs into the pores of MOFs.

Presently, the intercalation of ILs in MOFs, denoted as IL@MOF has gained widespread attention as a means to generate novel ionic hybrid composite materials [12]. Notable studies in this field include the exploration of a new class of proton conductors achieved through the incorporation of [VHim][HSO₄] (1-vinyl-3-hexylimidazolium hydrogensulfate) [VHim][TfO] (1-vinyl-3-hexylimidazolium triflate), and [VHim][TFSI] (1-vinyl-3-hexylimidazolium bis(trifluoromethylsulfonyl)imide) within MIL-101 [13]. Additionally, Xu et al. reported an optimal ionic conductivity of up to $6.21 \times 10^{-3} \text{ S}\cdot\text{cm}^{-1}$ at 150°C under a N₂ atmosphere by intercalating 1-ethyl-3-methylimidazolium thiocyanate, [EMIm][SCN], into MIL-101 [14]. In a recent study by Chen et al., a series of ILs consisting of the zwitterionic base EIMS (1-(1-ethyl-3-imidazolium)propane-3-sulfonate) and different inorganic and organic acids (e.g., SA = sulphuric acid, MSA = methanesulfonic acid, PTSA = p-toluenesulfonic acid) were synthesized and incorporated into MOF hybrid materials (SA-EIMS@MIL-101, MSA-EIMS@MIL-101, and PTSA-EIMS@MIL-101). These efforts resulted in an impressive σ value of up to $1.89 \times 10^{-3} \text{ S cm}^{-1}$ for SA-EIMS@MIL-101 [15]. Similarly, Sun et al. introduced a novel proton-conducting material, EIMS-HTFSA@MIL, by impregnating the binary IL EIMS-HTFSA (HTFSA = N,N-bis(trifluoromethanesulfonyl)amide) into the Metal-Organic Framework, MIL-101 [16]. These advancements underscore the significant potential of IL@MOF composites in enhancing the performance of future electrical energy storage systems.

Extensive research efforts have been directed toward developing MOF-based low-temperature Proton Exchange Membranes (PEMs), aiming to achieve high ionic conductivity under hydrous conditions below 100°C. However, there has been limited exploration of MOF-based PEMs under anhydrous conditions above 100°C. These materials hold the potential to be an alternative for the conventional middle or high-temperature PEMs in fuel cells. Furthermore, the structure interaction between MOFs and ILs and ionic transfer mechanism in such conditions remains largely unknown. In this study, a high-conductivity protic IL, known as diethylmethylammonium triflate ([Dema][TfO]) was introduced into the pores of a thermally stable MOF material, ZIF-8.

ZIF-8 offers several key advantages as a solid-state proton-conducting electrolyte for fuel cell applications. Its rigid yet flexible framework provides high thermal and chemical stability, enabling operation under intermediate to high temperatures and low-humidity or anhydrous conditions where conventional polymer electrolytes (e.g., Nafion) suffer performance loss. The uniform sodalite cages and tunable apertures facilitate the confinement of proton carriers such as water, acids, or protic ILs, forming continuous proton-conduction pathways while preventing electrolyte leakage. [Dema][TfO] offers several advantages over other ILs for ZIF-8 saturation, arising from its protic nature, suitable molecular size, and favorable interactions with the framework. As a protic IL, [Dema][TfO] supplies mobile protons that enable efficient proton transport through extended hydrogen-bond networks, resulting in higher proton conductivity than aprotic ILs. Its relatively compact and flexible ion structure is well matched to the pore dimensions of ZIF-8, allowing uniform infiltration and stable confinement within the cages without inducing framework collapse. Moreover, unlike strong Brønsted acids (e.g., H₃PO₄ and H₂SO₄), [Dema][TfO] delivers protons in a moderated manner that avoids aggressive attack on the ZIF-8 structure, thereby preserving the structural integrity of the ZIF-8 framework. The ionic conductivity of the IL@MOF composite was investigated in the temperature range from 60°C to 160°C. The experimental findings demonstrate that these hybrid composites exhibited exceptional thermal stability, relatively high ionic conductivity, and low activation energy. These results unequivocally substantiate the potential of IL@MOF hybrid composites as highly promising ionic conductors.

2 | Results and Discussion

2.1 | BET Measurements

To promote effective infiltration of the ionic liquid into the pores of ZIF-8, a capillary impregnation method was employed to encapsulate [Dema][TfO] within the framework, as illustrated in Figure 1a. As summarized in Table 1, the selected loading ratios correspond to theoretical pore-volume occupancies of approximately 20%, 40%, 60%, 80%, and 100% of the ZIF-8 porosity, respectively. A detailed description of the experimental procedure can be found in the Experimental section.

To determine the pore occupancy associated with the intercalation of [Dema][TfO] within the cage structure of ZIF-8, N₂ adsorption-desorption isotherm measurements were conducted on both pristine ZIF-8 and [Dema][TfO]@ZIF-8 at 77 K. In Figure 1b, it can be seen that both pristine ZIF-8 and [Dema][TfO]@ZIF-8 exhibit type I isotherms, that is a behavior characteristic of microporous materials. As depicted in Figure 1c and listed in Table 2, the BET surface areas of DT_{1.97}@Z, DT_{3.94}@Z, DT_{5.92}@Z, DT_{7.89}@Z, and DT_{9.86}@Z are found to be 776(12) m²/g, 626(10) m²/g, 123(2) m²/g, 9.1(1) m²/g, and 2.44(3) m²/g, respectively. These values are significantly reduced compared to the specific surface area of pristine ZIF-8, which amounts to 1452(22) m²/g. The (free) pore volume of DT_{1.97}@Z, DT_{3.94}@Z, DT_{5.92}@Z, DT_{7.89}@Z, and DT_{9.86}@Z can be calculated to $3382(33) \times 10^{-4} \text{ cm}^3/\text{g}$, $269(9) \times 10^{-4} \text{ cm}^3/\text{g}$, $50(4) \times 10^{-4} \text{ cm}^3/\text{g}$, $36.2(5) \times 10^{-4} \text{ cm}^3/\text{g}$, and $6.47(9) \times 10^{-4} \text{ cm}^3/\text{g}$, respectively. As

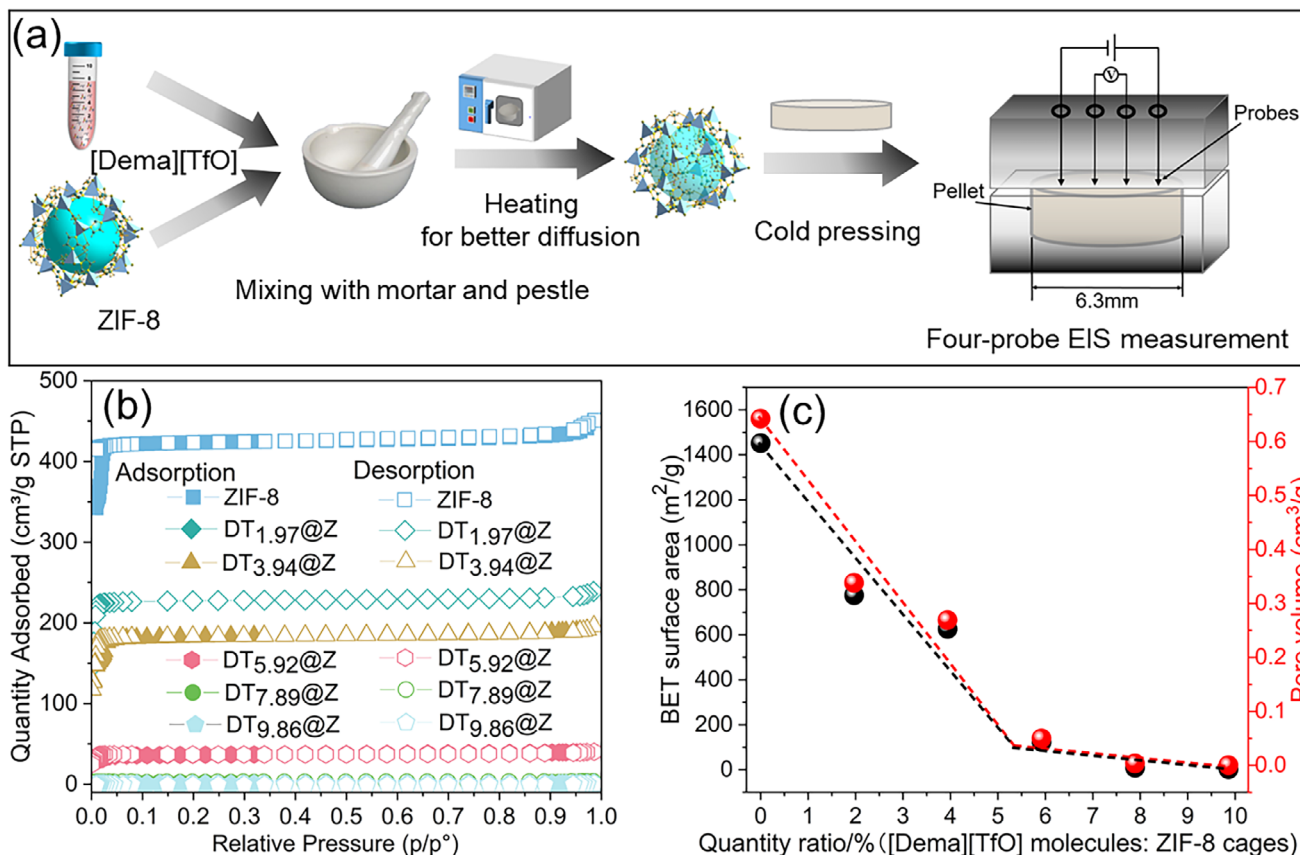


FIGURE 1 | (a) Flow chart of synthesis process and electrochemical impedance spectroscopy (EIS) of [Dema][TfO]@ZIF-8 composites, (b) N₂ adsorption-desorption isotherms of [Dema][TfO]@ZIF-8 at 77 K (STP: standard temperature and pressure), (c) Variation of BET specific surface area and pore volume with the quantity ratio ([Dema][TfO] molecules: ZIF-8 cages).

TABLE 1 | Components of [Dema][TfO]@ZIF-8 composites in this study.

Sample	[Dema][TfO]/ μL	ZIF-8/mg	Occupied pore volume ratio /%	Quantity ratio ([Dema][TfO] molecules: ZIF-8 sodalite cages)
ZIF-8	0	100	0	0:1
DT _{1.97} @Z	13.26	100	20	1.97:1
DT _{3.94} @Z	26.52	100	40	3.94:1
DT _{5.92} @Z	39.78	100	60	5.92:1
DT _{7.89} @Z	53.04	100	80	7.89:1
DT _{9.86} @Z	66.30	100	100	9.86:1

well, these values differ significantly from the pore volume of pristine ZIF-8, which is found to be $6630(89) \times 10^{-4} \text{ cm}^3/\text{g}$. Altogether, these observations affirm the presence of [Dema][TfO] ion pairs within the cage structure of ZIF-8. Pore blocking occurs when guest species occupy interconnected pores, thereby obstructing access to neighboring cavities and reducing the accessible surface area and pore volume measured by BET analysis. This effect can lead to an underestimation of the true surface area, as some pores become inaccessible to the adsorbate gas [17–19]. Consequently, the experimentally determined BET surface area and pore volume may deviate from theoretical values calculated based on the density of [Dema][TfO] and the pore volume of pristine ZIF-8.

2.2 | XRD Measurements

As depicted in Figure 2a, Powder X-ray diffraction (PXRD) analysis unveiled the emergence of new peaks positioned adjacent to the original ZIF-8 XRD peaks. Notably, the intensity of these new peaks increases while the original peaks progressively diminish with increasing [Dema][TfO] loading, as illustrated in Figure 2b. To evaluate the XRD pattern in detail, Rietveld refinement was utilized through Profex software, as exemplified in Figure S1. The results confirmed that pristine ZIF-8 exhibits a body-centred cubic structure with the space group $I\bar{4}3m$, with lattice parameters $a = 17.0230(2) \text{ \AA}$. In contrast, the diffractogram of

TABLE 2 | Pore structure properties of Parent ZIF-8 and [Dema][TfO]@ZIF-8.

Samples	BET surface area (m ² /g)	Pore volume (× 10 ⁻⁴ cm ³ /g)
ZIF-8	1452(22)	6630(89)
DT _{1.97} @Z	776(12)	3382(33)
DT _{3.94} @Z	626(10)	269(9)
DT _{5.92} @Z	123(2)	50(4)
DT _{7.89} @Z	9.1(1)	36.2(5)
DT _{9.86} @Z	2.44(3)	6.47(9)

the DT_{9.86}@Z sample can also be fitted using the same body-centred cubic structure with the space group I43m, but with slightly enlarged lattice parameters $a = 17.300(2)$ Å (+1.63%). This observation implies that the fundamental crystal structure of ZIF-8 remains unaltered, but the intercalation of [Dema][TfO] induces a modest expansion of the ZIF-8 sodalite cages.

The peaks corresponding to crystal planes (112), (222), and (431) have been deconvoluted to determine the phase ratio between newly formed and original peaks across all six samples, as depicted in Figures S2–S4. The evolving trends of the area ratios for these three sets of peaks exhibit strong consistency, as shown in Figure 2c. Notably, when the ratio of [Dema][TfO] molecules per ZIF-8 cage exceeds a threshold of approximately 5, the fraction of the newly formed phase increases more rapidly, whereas that of the original phase decreases sharply. Additionally, the pore volume decreases to a relatively low value at this threshold, as indicated in Figure 2c. Furthermore, an alteration in the PXRD reflection intensities was observed, with the relative intensity of the (100) peak decreasing while that of the (130) peak increases following the intercalation of [Dema][TfO] within the pores of ZIF-8. This phenomenon aligns with previous reports [16, 20, 21], suggesting a modification in the electron density within the ZIF-8 pores upon [Dema][TfO] introduction. The steady increase of an amorphous background indicates a fully random distribution of [Dema][TfO] molecules inside the pores of ZIF-8 [22, 23].

ZIF-8, characterized by a sodalite (SOD) topology, features narrow 6-ring windows with a diameter of 3.40 Å. These windows connect the large cavities of the ZIF-8 structure, which are roughly 11.6 Å in diameter and possess a pore volume of approximately 817 Å³. The van-der-Waals radii of the [Dema]⁺ cations and [TfO]⁻ anions are around 7.0 and 2.67 Å, respectively [24–26]. Theoretically, [Dema]⁺ cations are too large to enter the pores of ZIF-8. However, observations by experiment and simulation have shown that molecules that are theoretically too large to pass through the windows of the ZIF-8 framework, such as methane (3.84 Å for kinetic diameter) and nitrogen (3.60 Å for kinetic diameter), can still be adsorbed within the material, as demonstrated in previous literature [27, 28]. Additionally, it is reported that a substantial quantity of another IL consisting of a cation and anions with a size exceeding 3.4 Å, such as [EMIm][SCN], has been successfully introduced into the pores of ZIF-8 [14]. The encapsulation of large molecules inside the pores of ZIF-8 can be attributed to a phenomenon known as the ‘swing effect’ of the imidazole linkers.

The ‘swing effect’ of imidazolate linkers is characterized by the ability of the imidazolate ligands to rotate or ‘swing’ around the metal nodes within the MOF structure [29, 30]. This inherent flexibility of imidazolate linkers can result in alterations in the size and shape of the MOF’s pores. Previous work demonstrated that the I43m space group of ZIF-8 is maintained in a high-pressure phase. As pressure increases, additional solvent can be compelled into the nanopores, despite a reduction in the nanopore volume. Eventually, the sample undergoes a reorientation of the imidazolate linkers. This transition does not only facilitates the entry of more solvent into the original nanopores, but also enlarges the narrow channels connecting these pores. Consequently, there is an overall augmentation in porous volume and an increase in the size of the 6-ring windows [31]. Yu et al. reported that there are five different (rotational) orientations of the imidazolate linkers, resulting in five possible types of ZIF-8 apertures, whose windows of cages are 3.4, 4.1, 4.2, 4.7, and 6.9 Å [32]. The rotation of imidazolate linkers can lead to changes in the distance between the metal nodes, effectively causing the cages to expand, as shown in Figure 3. This theory aligns with our XRD results for [Dema][TfO]@ZIF-8. The ZIF-8 sodalite cages exhibit a non-monotonic expansion, resulting in two coexisting phases with different occupancy levels: a non-expanded phase with empty ZIF-8 cages, and an expanded phase with presumably maximum occupancy by [Dema][TfO] ion pairs. These two phases belong to the same space group, the modified intensity ratios of the XRD peaks represent the modified electron density.

The investigation of the nature of the interactions between guest molecules and zeolitic frameworks has been a topic of great interest. Previous studies offer valuable insights into this phenomenon, for example, Lee and colleagues observed a similar reversible insertion behavior for CO₂ introduced into the small-pore zeolite natrolite when subjected to a pressure of 1.5 GPa. This insertion results in a remarkable expansion of the unit cell volume of the host framework of approximately 6.8% [33]. The work by Haines et al. [34] and Coasne et al. [35] showed that at room temperature, CO₂ can be incorporated into the framework of the completely siliceous zeolite ZSM-5 (silicalite-1) with a pore size slightly larger than that of natrolite and that the presence of CO₂ in the pore stabilizes the zeolitic framework. Gao et al. documented an unconventional reversible displacive transition (6.4 Å) within the sodalite (SOD) cage of the flexible ZIF-65(Zn). Notably, ZIF-65(Zn) undergoes a distinctive stepwise II → III → I expansion, transitioning from an unusual ellipsoidal SOD cage (8.6 Å × 15.9 Å for II) to a spherical SOD cage (15.0 Å for I). The extent of the ZIF-65(Zn) expansion is contingent upon the polarity and geometry of the guest molecule. In the case of the non-polar linear molecule (n-hexane), a modest swelling from II to III occurs, attributed to host–guest hydrogen bonding interactions. Conversely, the polar branched molecule (iso-butanol) induces a substantial expansion from II to I, owing to the synergistic interplay of both host–guest and guest–guest hydrogen bonding interactions [36]. Furthermore, Dhumal et al. employed Density Functional Theory (DFT) calculations to elucidate a perturbation in the symmetry of the Cu-BTC MOF structure arising from the interaction between the IL anion (Ethyl sulfate [EtSO₄]⁻) and the Cu ions. The interaction specifically involves the oxygen atom of the anion and the Cu ion within the MOF, leading to an elongation of the Cu–Cu bond by 0.107 Å compared to its pure

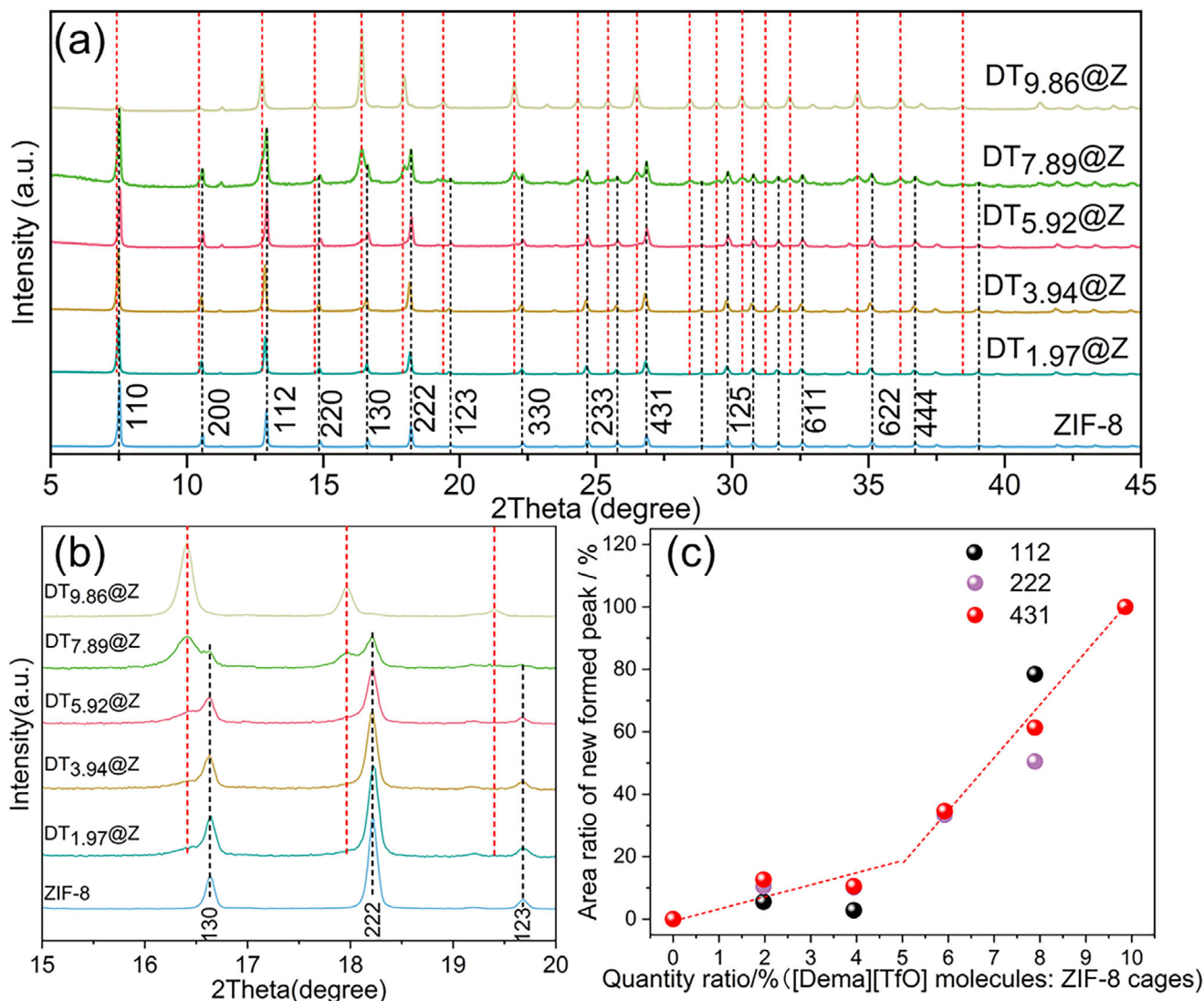


FIGURE 2 | (a) PXRD patterns of [Dema][TfO]@ZIF-8. (b) Magnification of Figure 2a,c. The relationship between the area ratio of newly formed peaks compared to the old peaks for crystal planes (112), (222), and (431) as a function of the quantity ratio ([Dema][TfO] molecules: ZIF-8 cages).

MOF counterpart, which has a bond length of 2.525 Å [37]. This would be an argumentation that the MOF-Structure is (partially) flexible regarding expansion.

2.3 | IR Spectroscopy

To further confirm the presence of [Dema][TfO] ion pairs within the pores of ZIF-8, Infrared (IR) spectra were recorded for both the pristine ZIF-8 and the [Dema][TfO]@ZIF-8 samples with varying composition, as illustrated in Figure 4a. Several characteristic peaks were identified in these spectra to reveal the molecular interactions and structural integrity. Specifically, the band at 420 cm⁻¹ can be attributed to the Zn–N stretching vibration within the ZIF-8 cage structure [38, 39]. This newly formed band located at around 417 cm⁻¹ is related to the Zn–N stretching vibration when [Dema][TfO] is introduced into the ZIF-8 cage structure, as revealed in Figure 4b. The intensity of the initial one decreases, and that of the new one increases when the amount of the [Dema][TfO] inside the cage increases. Figure S5 further

illustrates these changes by depicting the ratio of the newly formed peak area to the area of the Zn–N vibration peak. The area ratio (the area of the new formed peak: the area of the old peak) of the newly formed peak located at around 417 cm⁻¹ is 8.23%, 7.78%, 45.14%, 55.12% and 72.02% for DT_{1.97}@Z, DT_{3.94}@Z, DT_{5.92}@Z, DT_{7.89}@Z, and DT_{9.86}@Z, respectively, as indicated in Figure 4d. Furthermore, the peak positioned at 1584 cm⁻¹ corresponds to the C=N stretching vibration of ZIF-8, in good agreement with previously reported values [40–42]. Figure 4c displays the emergence of a new peak positioned to the right of the C=N stretching vibration peak, indicating a red-shift of 9.1 cm⁻¹ in the IR spectra of [Dema][TfO]@ZIF-8 when comparing to the pristine ZIF-8. The intensity of the initial peak related to the C=N stretching vibration decreases, and that of the new one increases when the amount of the [Dema][TfO] inside the cage increases.

The alteration in peak positions is indicative of structural modifications resulting from the interaction between [Dema][TfO] and ZIF-8. Figure S6 further illustrates these changes by depicting

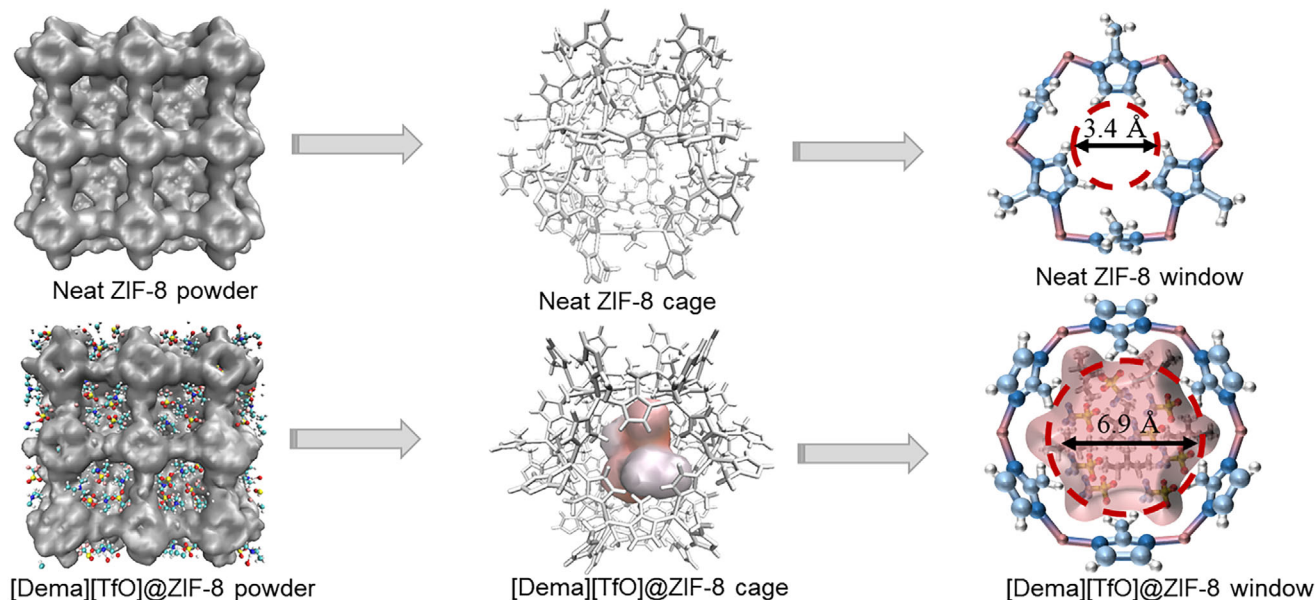


FIGURE 3 | Schematic diagram of the interaction between ZIF-8 and [Dema][TfO] ILs.

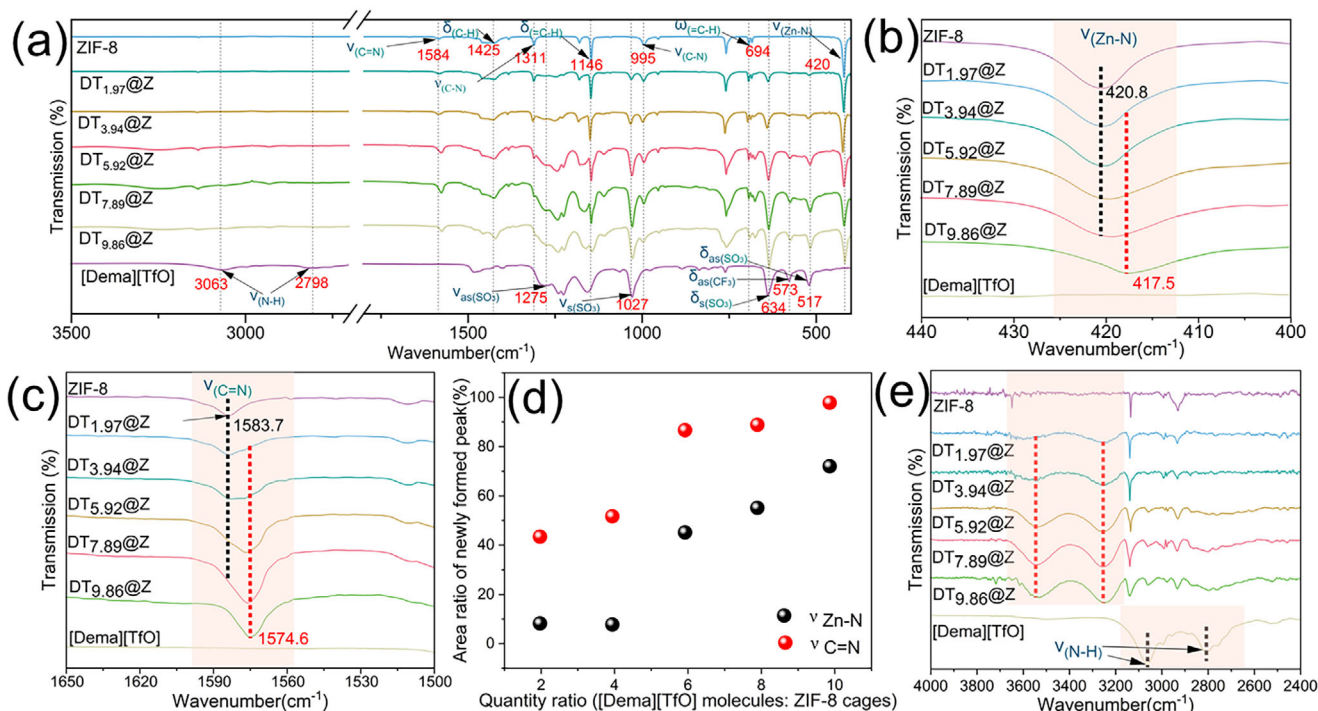


FIGURE 4 | (a) IR spectra of [Dema][TfO]@ZIF-8, IR spectra of (b) $\nu_{(Zn-N)}$ and (c) $\nu_{(C=N)}$ from ZIF-8 skeleton, (d) The relationship between the area ratio of newly formed peaks based on old peaks for $\nu_{(Zn-N)}$ and $\nu_{(C=N)}$ as a function of the quantity ratio ([Dema][TfO] molecules: ZIF-8 cages), (e) IR spectra of $\nu_{(N-H)}$ from [Dema][TfO] molecules.

the ratio of the newly formed peak area to the area of the C=N vibration peak. Remarkably, this area ratio exhibits an upward trend as the IL content increases, and the peak splitting analysis highlights this phenomenon. Specifically, Figure 4d shows for DT_{1.97}@Z, DT_{3.94}@Z, DT_{5.92}@Z, DT_{7.89}@Z, and DT_{9.86}@Z, the area ratios were measured as 43.4%, 51.7%, 86.7%, 88.9%, and 97.84%, respectively. These outcomes signify alterations in the

intramolecular C=N bonds within the imidazole ring of ZIF-8 as a consequence of its interaction with [Dema][TfO]. Collectively, these findings provide compelling evidence that [Dema][TfO] is indeed located inside the pores of ZIF-8, substantiating the success of the intercalation process. Interestingly, the turning point for the two peaks related to $\nu_{(Zn-N)}$ and $\nu_{(C=N)}$ occurred at about 5 ion pairs in one cage, as depicted in Figure 4d.

TABLE 3 | Wavenumber Assignment of IR for ZIF-8 and [Dema][TfO].

	Wavenumber (cm ⁻¹)	assignment		Wavenumber (cm ⁻¹)	assignment
ZIF-8	1584	$\nu_{(\text{C}=\text{N})}$	[Dema][TfO]	3063	$\nu_{(\text{N}-\text{H})}$
	1425	$\nu_{(\text{C}-\text{H})}$		2798	$\nu_{(\text{N}-\text{H})}$
	1311	$\nu_{(\text{C}-\text{N})}$		1275	$\nu_{\text{as}(\text{SO}_3)}$
	1146	$\delta_{(\text{C}=\text{H})}$		1027	$\delta_{\text{s}(\text{SO}_3)}$
	995	$\nu_{(\text{C}-\text{N})}$		634	$\delta_{\text{s}(\text{SO}_3)}$
	694	$\omega_{(\text{C}=\text{H})}$		573	$\delta_{\text{as}(\text{CF}_3)}$
	420	$\nu_{(\text{Zn}-\text{N})}$		517	$\nu_{\text{as}(\text{SO}_3)}$

Additionally, the band at 694 cm⁻¹ can be attributed to the =C–H wagging vibration (out-of-plane bending vibration) [38]. The peaks, observed for both ZIF-8 and [Dema][TfO]@ZIF-8 composites, appear at 995 and 1310 cm⁻¹, which correspond to the C–N bonds within the imidazole group of ZIF-8 [42–45]. These findings are succinctly summarized in Table 3. All of these characteristic peaks are also discernible in the spectrum of [Dema][TfO]@ZIF-8.

The peaks at 516 and 634 cm⁻¹ can be assigned to the asymmetric bending vibration of –CF₃ and the symmetric and asymmetric bending vibrations of –SO₃ in [Dema][TfO], see Figure 4a and Table 3. The peak at 573 cm⁻¹ can be assigned to the asymmetric bending vibration of –CF₃ in [Dema][TfO], see Figure 4a and Table 3. These results are in good agreement with the previous literature [46]. The peak of the symmetric stretching vibration of –CF₃ in [Dema][TfO] can be observed at 1027 cm⁻¹ [47]. The peaks at 3063 and 2798 cm⁻¹ can be assigned to the symmetric stretching vibration of N–H bonds in neat [Dema][TfO], see Figure 4e. Notably, these two N–H bond peaks shift to 3530 and 3250 cm⁻¹ positions after encapsulation within the pores of ZIF-8. The area ratios {(the peak at 3530 cm⁻¹): (the peak at 3250 cm⁻¹)} for DT_{1.97}@Z, DT_{3.94}@Z, DT_{5.92}@Z, DT_{7.89}@Z, and DT_{9.86}@Z, which were measured as 0.99, 1.30, 1.17, 1.03, and 1.14, respectively, are depicted in Figure S7 and are in close agreement with the area ratio (1.10) observed for neat [Dema][TfO].

In the context of the IR spectrum findings, it is crucial to highlight the significant influence of IL molecules on the vibrational modes of bonds within MOF cages. Mao et al. delved into the impact of elevated external pressure on the structure and stability of MOF α -Mg₃(HCOO)₆, employing in situ Fourier-Transform IR spectroscopy. The results revealed a noteworthy transformation: the peak associated with the asymmetric stretching vibration of O=C=O bifurcated into two distinct peaks until the external pressure reached 0.86 GPa. Subsequently, under 11.35 GPa, these peaks coalesced into a single entity. This transition was observed as reversible upon the restoration of normal pressure conditions [48]. As discussed above, the expansion of ZIF-8 cages is attributed to the framework's flexible apertures, which dynamically open through the reorientation of imidazolate linkers upon guest adsorption—a phenomenon commonly referred to as the “swing effect.” Specifically, the 2-methylimidazolate ligands rotate about the Zn–N coordination bonds, resulting in an expansion of the cage structure. Upon intercalation of

[Dema][TfO], the IR band corresponding to the Zn–N stretching vibration in ZIF-8 splits into two distinct modes at 420.8 and 417.5 cm⁻¹. The introduction of the highest loading of [Dema][TfO] results in a pronounced shift in the Zn–N stretching vibration band to a lower wavenumber, reaching 417.5 cm⁻¹ for DT_{9.86}@Z. At the highest loading level, a pronounced red shift of the Zn–N stretching vibration is observed, with the band centered at 417.5 cm⁻¹ for DT_{9.86}@Z, indicating significant framework expansion. At intermediate loadings (DT_{1.97}@Z, DT_{3.94}@Z, DT_{5.92}@Z, and DT_{7.89}@Z), both Zn–N stretching modes coexist, reflecting a mixed phase composed of unmodified and expanded ZIF-8 cages. This behavior suggests that the internal pressure exerted by confined IL molecules leads to elongation of the Zn–N bond lengths relative to their original values. Such bond elongation is consistent with the observations reported by He et al., who demonstrated that increases in bond length are typically accompanied by shifts to lower wavenumbers in vibrational spectra [49].

Previous mid-IR measurements conducted on an empty ZIF-8 framework revealed the remarkable sensitivity of the C=N stretching mode at 1584 cm⁻¹ to pressure, as evidenced by a significant red shift in the pressure range below 1.6 GPa [38]. The characteristic band splitting observed in the IR spectrum suggests an augmentation of intermolecular interactions [38]. In response to the observed redshift and the splitting of the C=N stretching mode at 1584 cm⁻¹ in the IR spectrum, it is noteworthy that the presence of [Dema][TfO] has a profound impact on the C=N bond of the ZIF-8 linker. Conversely, the stretching mode of the N–H hydrogen bond in [Dema][TfO] exhibits a blue shift of approximately 400–500 cm⁻¹, indicating that the constrained environment within the sodalite cages significantly impacts the hydrogen bonding of [Dema][TfO]. This shift is attributed to a faster vibrational frequency and a higher N–H bond strength as [Dema][TfO] enters the constrained environment. Chen et al. employed DFT simulations to investigate the vibrational modes of PILs composed of ammonium cations paired with different counter anions [50]. Their results show that shifts in the N–H stretching vibration of ammonium-based ILs are strongly dependent on the strength of cation–anion hydrogen bonding. Specifically, the formation of hydrogen bonds with the anion weakens the N–H bond, leading to a red shift of the N–H stretching band toward lower wavenumbers in the vibrational spectra. Parisi et al. performed an in-depth investigation of the IR spectrum of the PILs ([Dema][TfO]) by combining experimental

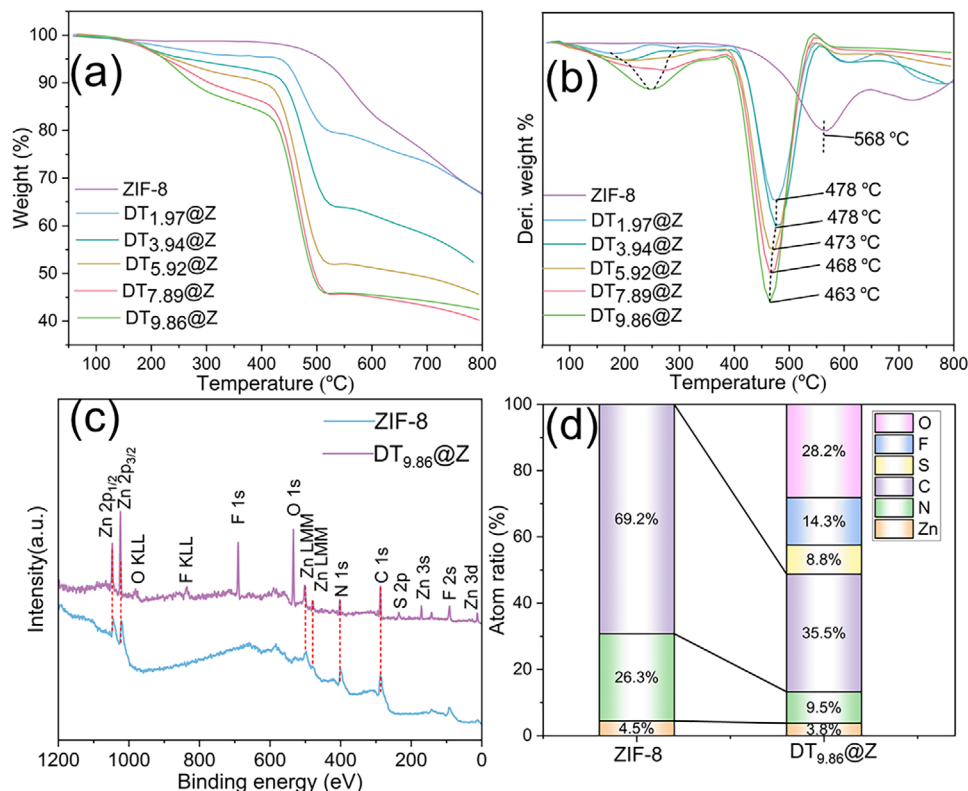


FIGURE 5 | (a) TGA of ZIF-8 and [Dema][TfO]@ZIF-8, (b) Change of derivative weight percent with increasing temperature, (c) XPS survey spectra of ZIF-8 and DT_{9.86}@Z, (d) Atom ratio of ZIF-8 and DT_{9.86}@Z calculated from the XPS survey spectra.

spectroscopy with atomistic simulations [51]. Their computational results demonstrate that the high-frequency vibrational modes associated with the N—H group are strongly influenced by the dynamic restructuring of the liquid. This behavior is corroborated by the observation of frequency shifts spanning approximately 400 cm⁻¹ for vibrations involving the shared hydrogen atom, reflecting the continuous modulation of hydrogen-bond strength caused by the dynamically changing local environment around the N—H moiety. Therefore, the observed blue shift of the N—H stretching vibration in [Dema][TfO] can be attributed to the disruption of interionic interactions between ion pairs confined in different cages, which weakens the original hydrogen-bond network and alters the local environment of the N—H group.

2.4 | TGA Measurements

The thermal properties of both pristine ZIF-8 and [Dema][TfO]@ZIF-8 were investigated via a thermogravimetric analysis (TGA), as illustrated in Figure 5a,b. The TGA curve of pristine ZIF-8 demonstrates a two-step weight loss occurring within the temperature range of 100 °C–800 °C. The TGA derivative curve reveals the minimum point at 568 °C for pristine ZIF-8. The result is in good agreement with the previous literature [52]. In contrast, the TGA curves for [Dema][TfO]@ZIF-8 exhibit a more intricate behavior, characterized by three sequential weight loss stages. The first two steps correspond to the loss of coordination water and the decomposition of [Dema][TfO]. There is an overlap observed between these peaks in each sample. The result is in agreement with the previous literature [53]. As

the quantity of intercalated [Dema][TfO] ion pairs increases, the temperature at which the water loss peak occurs shifts to higher temperature, while the [Dema][TfO] decomposition peak shifts to lower temperature. This shift in peak positions signifies alterations in the thermal behavior associated with [Dema][TfO] intercalation.

Figure S8 illustrates the weight loss variation as a function of the quantity of [Dema][TfO] ion pairs. The weight attributed to bonded water increases from 1.2% to 7.9% due to the pronounced water-absorbing capability of [Dema][TfO]. It is noteworthy that the decomposition temperature of pure [Dema][TfO] is within the range of 350 °C–400 °C [54]. However, this temperature range decreases to 250 °C–300 °C when [Dema][TfO] is encapsulated within the pores of ZIF-6. Meanwhile, the weight loss of [Dema][TfO] determined by TGA amounts to 1.6%, 2.0%, 2.8%, 5.3%, and 7.4% for DT_{1.97}@Z, DT_{3.94}@Z, DT_{5.92}@Z, DT_{7.89}@Z, and DT_{9.86}@Z, respectively. A noticeable trend emerges upon comparing these results to pristine ZIF-8 (decomposition temperature ~568 °C), indicating a discernible shift toward lower temperatures upon the incorporation of [Dema][TfO]. Specifically, the decomposition peak of [Dema][TfO]@ZIF-8 declines from 478 °C to 463 °C with increasing quantities of intercalated [Dema][TfO] ion pairs. The thermal analysis highlights the influence of the [Dema][TfO] encapsulation on the thermal behavior of the composite material.

IR results imply an intensified interaction between the ZIF-8 framework's imidazole rings and the guest [Dema][TfO] ion pairs within the unit cell. This alteration of the Zn—N and

C=N stretching mode can likely be attributed to the weakening of π -bonds within the imidazolate rings, which arises from a subtle distortion of the imidazole ring structure [38]. As we know, stronger π -bonds are associated with higher stability and, consequently, higher decomposition temperatures. Weaker π -bonds are more susceptible to breaking at lower temperatures, which can lead to the decomposition of the molecule. Therefore, we deduced that the decrease in the decomposition temperature of ZIF-8 from 568°C to 463°C is partly related to the weakening of the π -bond induced by cage expansion. Nozari et al. similarly encapsulated the IL [EMIM][TFSI] within the porous interior of ZIF-8 [55]. Their results showed that incorporation of the IL into the ZIF-8 pores leads to a reduction in the thermal decomposition temperature. This behavior was attributed to the disruption of unstable configurations within the framework, arising from modified Zn^{2+} -N coordination and interactions induced by the confined IL, which collectively shorten the lifetime of thermally labile structures.

The TGA results indicate that the decomposition temperature of [Dema][TfO] decreases when the IL is confined within the ZIF-8 cages. This reduction is primarily attributed to the disruption of interionic interactions between ion pairs distributed across different cages, which weakens the original hydrogen-bond network. Additionally, the spatial confinement and strong host-guest interactions imposed by the ZIF-8 framework restrict the structural rearrangements of the IL, making it more susceptible to thermal decomposition at lower temperatures. These findings highlight how confinement not only alters the physical arrangement of the IL but also modulates its thermal stability and potentially its transport properties within the MOF structure.

2.5 | XPS Measurements

The compositions of the sample pellets were characterized by XPS, monitoring a wide binding energy range of 0 to ~1200 eV, encompassing the regions of Zn-2p, F-1s, O-1s, N-1s, C-1s, S-2s and S-2p for neat ZIF-8 and the $\text{DT}_{9.86}\text{@Z}$ pellet. Figure 5c illustrates a typical survey spectrum of a ZIF-8 pellet. All expected features of ZIF-8 were observed, including zinc (coordinating metal), nitrogen (imidazole), and carbon (imidazole). The surface composition of the neat ZIF-8 sample is as follows: Zn 4.5 at%, N 26.3 at%, and C 69.2 at%, as indicated in Figure 5d.

Figure 6a shows that the XPS spectrum of Zn displayed the doublet of Zn-2p_{1/2} and Zn-2p_{3/2} at 1045.6 eV and at 1022 eV, respectively, thus confirming the +2 oxidation state of Zn [56]. The separation between the main peak and the adjacent peak was about 2–3 eV, respectively. The adjacent peaks located at 1038.7 and 1017.1 eV are unclear. Tian et al. reported that the adjacent peak is regarded to correspond to satellite [57]. A well-fitting result of the N-1s spectra was achieved by employing two peaks of the ZIF-8 pellet, as illustrated in Figure 6b. The main peak, situated at 402.1 eV, was attributed to the imidazole groups in agreement with the result in former literature. An additional smaller peak was observed at 395.6 eV, which is indicative of the presence of secondary amines [58]. Secondary amines may appear from an amount of uncoordinated methylimidazole linkers [57]. Moreover, as indicated in Figure 6c, the fitted XPS C-1s spectrum includes the C–C/C–H, C=C peaks with binding energies of

284.3 eV, the C=N, C–N–C peaks with binding energies of 286.7 eV, respectively [59, 60].

A typical survey spectrum of a $\text{DT}_{9.86}\text{@Z}$ sample is illustrated in Figure 5c. All expected features of ZIF-8 and [Dema][TfO] were observed, including zinc (coordinating metal), nitrogen (imidazole and [Dema][TfO]), carbon (imidazole and [Dema][TfO]), sulphur ([Dema][TfO]), and fluorine ([Dema][TfO]). The atom ratio of the $\text{DT}_{9.86}\text{@Z}$ sample is shown in Figure 5d. The surface composition of the $\text{DT}_{9.86}\text{@Z}$ sample is as follows: Zn 3.8 at%, N 9.5 at%, C 35.5 at%, S 8.8 at%, F 14.3 at%, and O 28.2 at% as indicated in Figure 5d. The XPS spectrum of Zn, showing the characteristic doublet peaks of Zn 2p at 1045.2 eV (Zn 2p_{1/2}) and 1022.0 eV (Zn 2p_{3/2}) for the $\text{DT}_{9.86}\text{@Z}$ sample, is illustrated in Figure 6d. Notably, the area ratio of the unsaturated zinc node peak in $\text{DT}_{9.86}\text{@Z}$ decreased compared to that in the neat ZIF-8 sample. The XPS N-1s spectrum was deconvoluted into three peaks situated at 399.5, 400.8, and 402.4 eV, see Figure 6e. The peaks at 400.8 eV and 402.4 eV correspond to nitrogen in the 2-methylimidazole ring and C–N in [Dema][TfO], respectively, consistent with prior findings [61]. The absence of the secondary amine-related peak is attributed to the reaction between the unsaturated zinc nodes and secondary amines during the capillary action process at 105°C [57]. Additionally, the peak at 401.5 eV is likely associated with [Dema]⁺ trapped within the ZIF-8 cages, which corroborates the results obtained from IR analysis. The peaks at 285.1 eV and 286.5 eV can be assigned to represent C–C/C=C and C–N in the [Dema][TfO]/ZIF-8 composites, see Figure 6f [62–64]. The peak at 532.2 eV in the O-1s spectrum can be ascribed to C–SO₃ in [Dema][TfO], see Figure 6g [65]. The peak at 688.6 eV in the F-1s spectrum is reported to correspond to the C–F group in [Dema][TfO], see Figure 6h [66]. As illustrated in Figure 6i, the XPS S-2p spectrum can be further deconvoluted into two peaks located at 169.7 eV and 168.7 eV, which are related to S-2p_{3/2} and S-2p_{1/2} in the C–SO₃ group, respectively [67, 68].

2.6 | ¹H- and ¹⁹F-NMR Measurements

The nuclear magnetic resonance (NMR) spectra of the [Dema][TfO]/ZIF-8 samples are shown in Figure 7. Considering the ¹H-NMR spectra, only a single set of signals can be observed up to an uptake of 7.89 ion pairs per sodalite cage. Beyond this level, two distinct sets of signals appear. This observation is corroborated by the ¹⁹F-NMR results, which align with the ¹H findings, indicating that [Dema][TfO] ion pairs are incorporated exclusively within the sodalite cages below this uptake level. At higher uptake levels, a portion of the [Dema][TfO] ions likely resides in a secondary environment, possibly within the grain boundaries.

Typically, the proton resonance of X–H shifts to a higher chemical shift (downfield) compared to non-hydrogen-bonded X–H [69]. This downfield shift arises from strong deshielding of the proton, caused by electron density redistribution around the hydrogen atom upon hydrogen bond formation. In our case, the newly formed peaks appear at lower chemical shifts compared to the original peak of bulk [Dema][TfO]. This indicates that [Dema][TfO] has entered the ZIF-8 cages, leading to disruption of the original hydrogen-bond network. These observations are consistent with the IR results, which show a corresponding

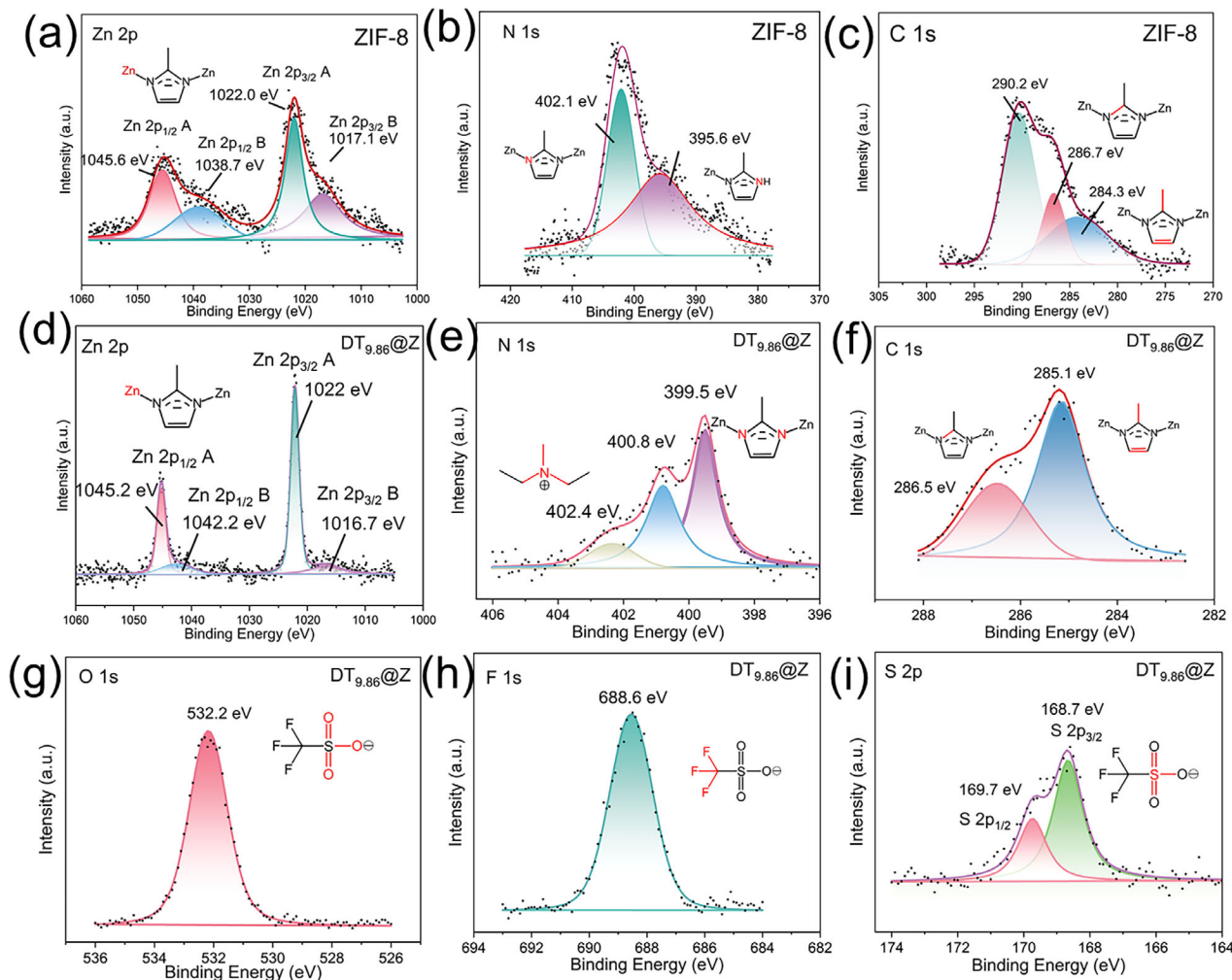


FIGURE 6 | High-resolution XPS spectra (a) Zn-2p, (b) N-1s, (c) C-1s of ZIF-8, (d) Zn-2p, (e) N-1s, (f) C-1s (g) O-1s, (h) F-1s, (i) S-2p of the sample DT_{9.86}@Z.

shift of the N–H stretching vibration to higher wavenumbers, further confirming the weakening of hydrogen bonding upon confinement.

2.7 | (Total) Ionic Conductivity/EIS Measurements

Neat [Dema][TfO] has a high ionic conductivity of $5.3 \times 10^{-2} \text{ S cm}^{-1}$ at 150°C and $1.0 \times 10^{-2} \text{ S cm}^{-1}$ at room temperature under anhydrous conditions (total cationic and anionic conductivity) [54]. The ionic conductivity of the [Dema][TfO]@ZIF-8 composites was studied by alternating current (AC) impedance measurements at temperatures ranging from 160°C to 60°C , employing pellet-shaped samples for testing. As shown in Figure 8a, the Nyquist plots of DT_{7.89}@Z from 160°C to 60°C exhibit well-defined Debye semicircles or arc-shaped curves at high frequencies, corresponding to the electrolyte impedance. The capacity is between 3.6×10^{-11} and $3.9 \times 10^{-11} \text{ F}$ and the characteristic frequency is between 15 kHz and 400 MHz at different temperature for DT_{7.89}@Z. At low frequencies, a tail appears which is attributed to Warburg diffusion [70].

The equivalent circuit used for fitting the impedance data of the [Dema][TfO]@ZIF-8 composites at 60°C to 160°C consists of an RC-circuit and a Warburg element. The RC-circuit is related to the impedance of electrolyte, that is $R_{\text{DTx@Z}}$ and C_{bulk} [71]. The resistance $R_{\text{DTx@Z}}$ of the [Dema][TfO]@ZIF-8 composites is decreasing with increasing temperature and the quantity ratio of [Dema][TfO] molecules to ZIF-8 cages. Thus, the ionic conductivity increases with increasing temperature and quantity ratio of [Dema][TfO] ion pairs to ZIF-8 cages. In Figure 8b, it is illustrated that the total conductivity experiences a dramatic decrease when the quantity ratio of [Dema][TfO] ion pairs to ZIF-8 cages is below approximately 5. This finding aligns with the turning point indicated by the results of BET, XRD, and IR measurements. Furthermore, as listed in detail in Table 4, the maximum conductivity observed for DT_{9.86}@Z, reaches a value of $1.09(6) \text{ mS cm}^{-1}$ at 160°C . The conductivity of neat [Dema][TfO] is 53 mS cm^{-1} at 150°C and 10 mS cm^{-1} at room temperature under anhydrous conditions [54]. In contrast, the conductivity of [Dema][TfO]@ZIF-8 is an order of magnitude lower than that of pure [Dema][TfO].

The activation energies E_a were computed for the composites by using the Arrhenius equation, as shown in Figure 8c. The

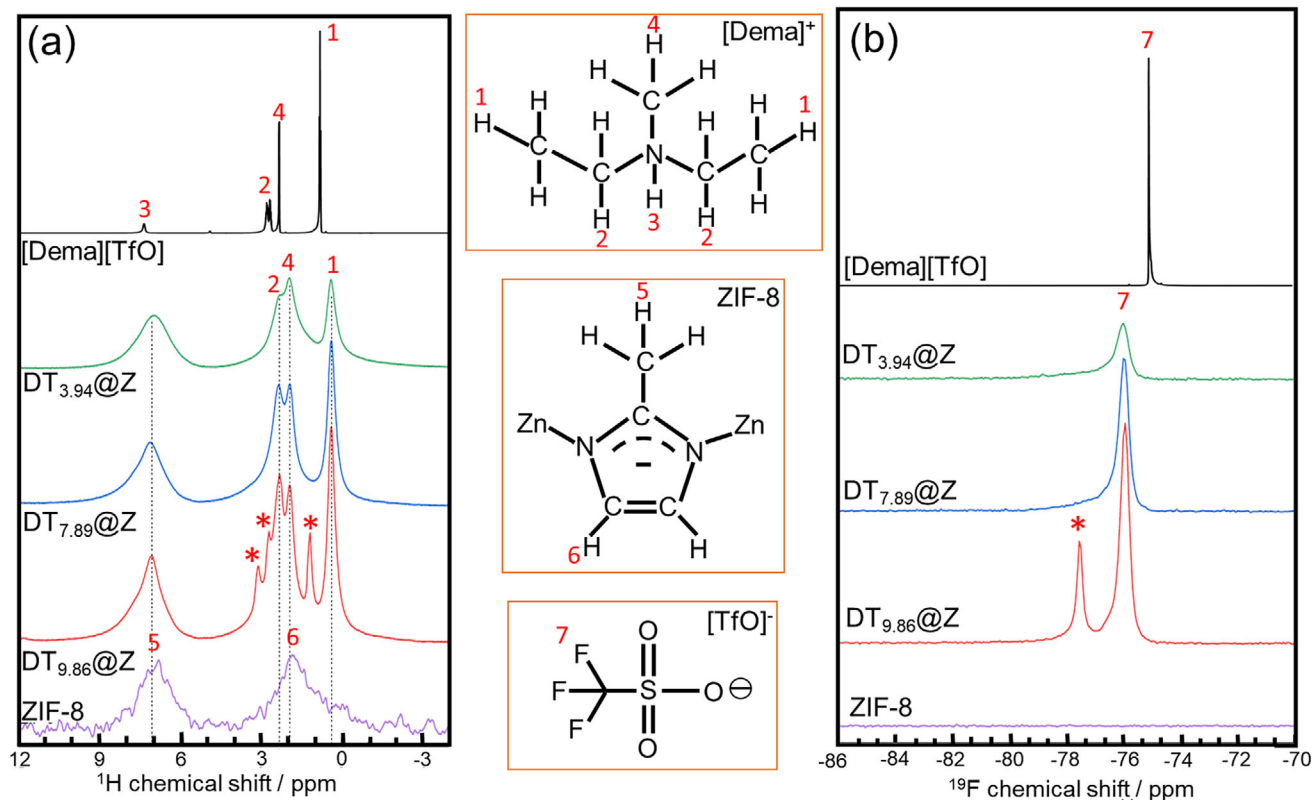


FIGURE 7 | ^1H and ^{19}F -NMR spectra of neat ZIF-8 and [Dema][TfO], as well as of DT_{3.94}@Z, DT_{7.89}@Z and DT_{9.86}@Z samples (* represents the newly formed peak).

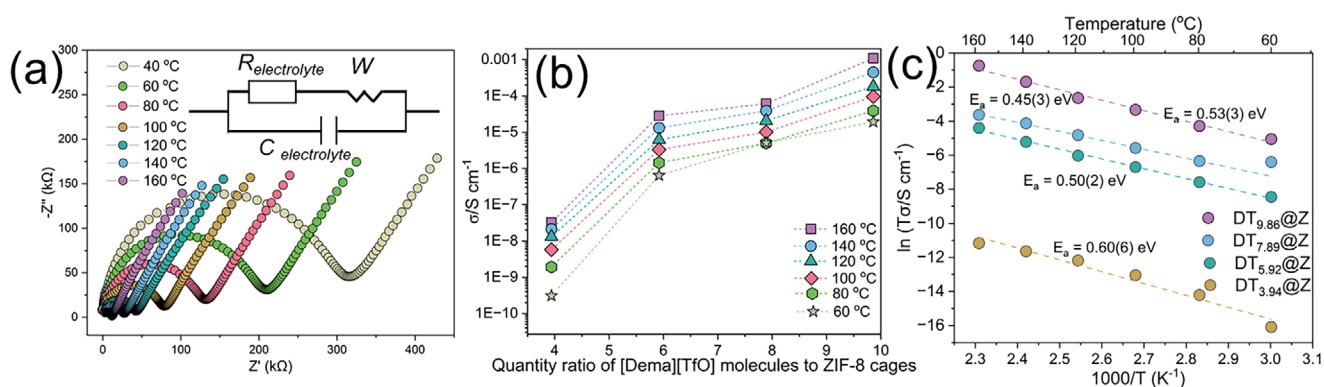


FIGURE 8 | (a) Temperature dependent impedance spectra conductivities of [Dema][TfO]@ZIF-8 composites as a function of the quantity ratio of [Dema][TfO] molecules to ZIF-8 cages, (b) Total conductivity and (c) Activation energy for various concentrations of [Dema][TfO]@ZIF-8 samples.

TABLE 4 | Ionic conductivity for various concentrations of [Dema][TfO]@Z at different temperatures under anhydrous conditions.

T (°C)	DT _{3.94} @Z (mS cm ⁻¹)	DT _{5.92} @Z (mS cm ⁻¹)	DT _{7.89} @Z (mS cm ⁻¹)	DT _{9.86} @Z (mS cm ⁻¹)
160	$3.27(2) \times 10^{-5}$	$2.83(4) \times 10^{-2}$	$6.11(2) \times 10^{-2}$	1.09(6)
140	$2.13(1) \times 10^{-5}$	$1.31(6) \times 10^{-2}$	$3.90(2) \times 10^{-2}$	$4.45(1) \times 10^{-1}$
120	$1.31(6) \times 10^{-5}$	$6.14(1) \times 10^{-3}$	$2.05(5) \times 10^{-2}$	$1.81(3) \times 10^{-1}$
100	$5.80(3) \times 10^{-6}$	$3.29(4) \times 10^{-3}$	$1.01(2) \times 10^{-2}$	$9.58(6) \times 10^{-2}$
80	$1.92(2) \times 10^{-6}$	$1.43(4) \times 10^{-3}$	$4.98(2) \times 10^{-3}$	$3.89(2) \times 10^{-2}$
60	$3.09(1) \times 10^{-7}$	$6.41(6) \times 10^{-4}$	$5.06(2) \times 10^{-3}$	$1.92(3) \times 10^{-2}$

values for activation energy E_a of the [Dema][TfO]@ZIF-8 composites were determined using Equation 2, yielding the following results: 0.53(3) eV ($DT_{9.86}@Z$), 0.45(3) eV ($DT_{7.89}@Z$), 0.50(2) eV ($DT_{5.92}@Z$), and 0.60(6) eV ($DT_{3.94}@Z$). The activation energy of pure [Dema][TfO] is 0.207 eV under anhydrous conditions [72].

The calculations of activation energies aimed to provide insights into the underlying proton-conduction mechanisms. The activation energy varied within the range of 0.45(3) eV to 0.60(6) eV for the [Dema][TfO]@ZIF-8 composites. Several studies corroborate the findings within this range. Chen et al. incorporated PTSA-EIMS (PTSA = p-toluenesulfonate acid, EIMS = 1-(1-ethyl-3-imidazolium)propane-3-sulfonate) within the pores of MIL-101, revealing an activation energy of 0.432 eV [15]. Additionally, Fujie et al. synthesized a composite comprising EMI-TFSA (1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide) and ZIF-8, with an associated activation energy of 0.35 eV [73]. The activation energy of neat [Dema][TfO] is reported to be 0.207 eV under anhydrous conditions [72]. However, the diffusion of [Dema][TfO] ion pairs is significantly hindered when confined within the cages of ZIF-8, requiring higher activation energy for transport. This can be attributed to the restricted environment of the sodalite cages, which limits the mobility of the IL molecules and increases the energy barrier for migration between neighboring cages. As a result, the activation energy for ion transport rises to the range of 0.45(3) to 0.60(6) eV. The confinement not only slows translational diffusion but also affects the reorganization of hydrogen-bond networks within the IL, further contributing to the increased activation barrier [74]. Despite this, the confined [Dema][TfO] maintains sufficient proton mobility to support solid-state conduction, highlighting a trade-off between enhanced structural stability and slightly reduced ion transport compared with the bulk IL. Understanding this balance is critical for optimizing the design of MOF-based solid-state proton-conducting electrolytes.

Several studies in the literature provide evidence supporting this confinement phenomenon. Kanj et al. explored the conduction properties of an IL, specifically 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide ([BMIM][TFSA]) within the regular pores of the relatively rigid and crystalline HKUST-1 metal-organic framework. The findings revealed that under high loadings, both anions and cations are compelled to occupy the same pore windows simultaneously. Due to the restricted pore size of the MOF, preventing the simultaneous passage of both ions, the opposing drift directions of the ions result in mutual blockage and a transient jamming of the pore windows [75]. Tang employed molecular dynamics (MD) simulations to investigate the diffusion behavior of water molecules confined within ZIF-8 [76]. The study revealed that the self-diffusion coefficient of water inside the ZIF-8 cages is typically one to two orders of magnitude lower than that of bulk water. This pronounced reduction in mobility is primarily attributed to the restricted pore size and the strong confinement effects imposed by the rigid ZIF-8 framework, which limit both translational and rotational motion of the water molecules. Schmidt et al. performed a comprehensive thermodynamic and kinetic study to investigate ethane diffusion within ZIF-8 [77]. Their results revealed that diffusion is a hindered process, controlled by a transition state in which an ethane molecule must pass through the cage aperture

(or “gate”) formed by the 2-methylimidazole linkers connecting adjacent ZIF-8 cages. This gating process imposes a significant energy barrier that dominates the overall diffusion dynamics, highlighting the critical role of the framework’s flexible linkers in regulating molecular transport within the ZIF-8 structure. Future work should explore a broader range of ionic liquids and MOF hosts. In particular, different types of ionic liquids could be incorporated into MOFs with larger cages and wider windows. Such combinations may provide additional opportunities to enhance ionic conductivity and reduce the activation energy for ion transport, thereby expanding the scope and diversity of the IL@MOF system.

3 | Conclusions

In summary, we have successfully synthesized ionic conductive materials by intercalating [Dema][TfO] into the pores of ZIF-8. This material exhibits several key characteristics and advantages: The structural integrity of ZIF-8 remains unchanged, yet the cages of ZIF-8 experience an expansion of approximately 0.277 Å upon the encapsulation of [Dema][TfO] ion pairs. The expansion can be most probably attributed to the swinging effect of the organic ligand, while the decrease in decomposition temperature can be ascribed to the weakened π -bond resulting from the expansion of ZIF-8 cages. Once the quantity ratio of [Dema][TfO] ion pairs to ZIF-8 cages increases, the area ratio of newly formed XRD and IR peaks and total conductivity increase, while the pore volumes decrease significantly. Up to 7.89 calculated occupation [Dema][TfO] can reside in the cages. For high calculated uptake, part of the [Dema][TfO] can be found in a second environment, presumably in grain boundaries. The ionic conductivity of $DT_{9.86}@Z$ samples exhibits total conductivity reaching up to 1.09(6) mS cm⁻¹ at 160°C. Most importantly, we find that confinement within ZIF-8 disrupts the hydrogen-bond network of [Dema][TfO] and increases the activation energy for proton transport. Nevertheless, immobilizing the ionic liquid inside the ZIF-8 pores is worthwhile, as the benefits, such as stable confinement, continuous conduction pathways, and prevention of leakage, outweigh the drawbacks of hydrogen-bond disruption and the modest increase in activation energy. Furthermore, the fabrication method is practical and feasible, offering a promising method for the production of novel composite electrolytes involving other ILs and MOFs.

[Dema][TfO]@ZIF-8 shows strong potential as a solid-state proton-conducting electrolyte because the protic IL [Dema][TfO] supplies mobile protons for efficient proton transport, while confinement within the ZIF-8 framework creates continuous conduction pathways and suppresses electrolyte leakage. The hydrogen-bond networks formed by the confined ILs enable anhydrous proton conduction, allowing stable operation under low-humidity and intermediate-temperature conditions where conventional polymer electrolytes often perform poorly. Moreover, the rigid ZIF-8 host imparts mechanical stability, thermal robustness, and improved safety. Nevertheless, further studies are required to optimize proton conductivity, long-term stability, and scalability, indicating that substantial development is still needed before practical application in solid-state fuel cells, electrochemical sensors, and related proton-based energy conversion devices.

4 | Experimental Section

ZIF-8 MOF (Zeolitic imidazolate framework-8, Basolite Z1200) and [Dema][TfO] were purchased from Merck KGaA. [Dema][TfO] went through a vacuum dehydration process at 60°C for 12 h, while the ZIF-8 was subjected to vacuum activation at 105°C for 12 h to eliminate undesirable guest molecules.

The synthesis of [Dema][TfO]@ZIF-8 was accomplished by using the capillary action method, with a quantity ratio of [Dema][TfO] ion pairs to ZIF-8 cages as follows: 1.97:1, 3.94:1, 5.92:1, 7.89:1 and 9.86:1. According to Table 1, these ratios were chosen to obtain a theoretical pore volume of ZIF-8 by 20%, 40%, 60%, 80% and 100%, respectively. These calculations were performed in accordance with Equations S1–S5, and further detailed information is provided in Table S1. The volume occupancy was derived from pore volume measurements of ZIF-8 (0.663 cm³/g) by performing a Brunauer–Emmett–Teller (BET) analysis and from the bulk density of [Dema][TfO] (1.292 g/cm³) [78]. In a representative synthesis shown in Figure 1a, 66.3 μL of [Dema][TfO] and 100 mg of dehydrated ZIF-8 were mixed using a mortar and pestle. Subsequently, the resulting powders were dried overnight under vacuum conditions at 105°C. This particular sample, denoted as DT_{9.86}@Z, represented the ratio of 9.86 [Dema][TfO] ion pairs and one ZIF-8 cage (1/2 crystallographic unit cell) on average. A similar procedure was employed to prepare the other samples denoted as DT_x@Z, with *x* values corresponding to 1.97, 3.94, 5.92, and 7.89. In Table S2, ICP-OES results are shown, verifying that the actual elemental content is consistent with the theoretical content.

Powder X-ray diffraction (PXRD) of the samples was performed by using a Bruker D8 Advanced diffractometer, employing Cu-K_α radiation ($\lambda = 1.5418 \text{ \AA}$). The diffractograms were evaluated by Rietveld refinement, employing the Profex software [79]. IR spectroscopy analyses were conducted using a Nicolet spectrometer with a GladiATR ATR unit, spanning the wavenumber range of 400 to 4000 cm^{−1}. The determination of nitrogen adsorption and desorption isotherms (BET) was performed at 77 K (Micromeritics Gemini VII). X-ray photoelectron spectroscopy (XPS) analysis was performed using the cluster tool established by the Institute of Energy Materials and Devices – Photovoltaics (IMD-3), Forschungszentrum Jülich with a Multiprobe MXPS system from Scienta Omicron involving an ARGUS hemispherical electron spectrometer. An XM1000 AlK_α x-ray source at 300 W is used. All spectra are collected in constant Analyzer-Energy (CAE) mode with a path energy (PE) of 100 eV for the survey spectrum and 20 eV for the high-resolution spectra. The resulting data were calibrated by using the Zn-2p peak at 1022 eV and fitted by employing the software XPS-peak 4.1 (<http://xpspeak.software.informer.com/4.1/>) and Igor Pro (Wavemetrics) with XPST Plugin by Martin Schmid (<https://www.wavemetrics.com/project/XPSTools>). Thermal gravimetric tests, using STA 449 F1 Jupiter simultaneous thermogravimetric analyzer, were carried out by ramping the temperature from room temperature to 800°C at a rate of 10°C min^{−1}, maintaining a constant gas flow of 50 mL/min. Nuclear magnetic resonance (NMR) spectra of pure [Dema][TfO] were obtained with a liquid probe at a 300 MHz spectrometer on a Bruker AVANCE NEO instrument. Solid-state MAS-NMR experiments were performed on the instrument equipped with a magic-angle-

spinning (MAS) probe supporting rotors (2.5 mm) at a 500 MHz spectrometer.

For conductivity measurements, compacted samples were prepared as pellets with dimensions of 6.3 mm in diameter and 1.5 mm in thickness. These pellets were fabricated by applying a pressure of 5 MPa to the powders. Alternating-current (AC) impedance measurements were conducted utilizing a four-probe method (as shown in Figure 1a), employing platinum-probe electrodes and an electrochemical workstation (Zahner Zennium) within a frequency range extending from 10 mHz to 1 MHz. To eliminate any potential influence of absorbed trace water on proton conductivity, the pellets were maintained at 160°C under an anhydrous atmosphere for 6 h. Subsequently, the conductivity of each sample was recorded as the temperature was lowered from 160°C to 60°C under anhydrous atmosphere. At each temperature, an Electrochemical Impedance Spectroscopy (EIS) measurement was conducted three times, with a 5 h interval between each test. Based on a four-probe measurement, the overall conductivity (σ/S) of the sample was determined using Equation 1 [80].

$$\sigma = \frac{1}{2\pi rR} \quad (1)$$

where σ is the overall conductivity, r is the distance of the two probes, and R is the measured resistance from impedance spectroscopy. It is worth noting that the ionic conductivity of all the samples exhibited an Arrhenius behavior, characterized by an increase in conductivity with rising temperature. The activation energy E_a for proton transport, expressed in eV, was computed by fitting the proton conductivity data according to the Arrhenius equation (Equation 2):

$$\sigma T = \sigma_0 e^{-\frac{E_a}{k_B T}} \quad (2)$$

where k_B is the Boltzmann constant, and T is the temperature.

Author Contributions

Wen Yang: conceptualization, investigation, writing – original draft, methodology, writing – review and editing. **Christian Rodenbücher:** supervision, conceptualization, writing – review and editing. **Sylvio Indris:** methodology, writing – review and editing. **Benjamin Klingebiel:** writing – review and editing, methodology. **Mareen Schaller:** methodology. **Nan Sun:** methodology. **Jiangshui Luo:** conceptualization, supervision, writing – review and editing. **Carsten Korte:** conceptualization, writing – review and editing, supervision, methodology, funding acquisition.

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Conflicts of Interest

The authors declare no conflicts of interest.

Data Availability Statement

The data that support the findings of this study are available on request from the corresponding author. The data are not publicly available due to privacy or ethical restrictions.

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Supporting Information

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