Infrared Spectroscopy of Polybenzimidazole in the Dry and Hydrate Forms: A Combined Experimental and Computational Study

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Abstract: In the present article, the infrared spectrum of polybenzimidazole (PBI) in the dry and hydrate forms has been studied both experimentally and theoretically to improve the interpretation of its complex features, especially in the \( \nu(\text{NH})/\nu(\text{OH}) \) range, which is extensively affected by sorbed water and temperature. Time-resolved Fourier-transform infrared spectroscopy measurements were performed to monitor \( \text{H}_2\text{O} \) sorption, whereas the temperature behavior was investigated by in situ measurements in the 100–450 °C range. Density functional theory calculations on simplified models of dry and hydrated PBI showed good agreement with experimental results and allowed a reliable interpretation of the observed effects. The combined experimental/computational analysis provided relevant structural information which suggested the possibility of modifying the diffusion properties of PBI and motivated further experimental activities.

1. INTRODUCTION

Polybenzimidazole [poly(2,2′-(m-phenylene)-5,5′-bibenzimidazole, PBI] is a high-performance technopolymer well-known for its outstanding properties. It exhibits the highest \( T_g \) among organic polymers (425–436 °C), good resistance to solvents and corrosive chemicals, flame resistance, and an exceptional thermal and thermo-oxidative stability (decomposition temperature approaching 600 °C).\(^1\)–\(^3\) PBI has been successfully employed in numerous applications requiring exposure to extreme conditions, such as in aerospace and in the fabrication of protective apparel such as firefighters’ gear and astronauts’ suits. However, more recent applications for PBI have focused on its usability for membrane separations. Initially, it was employed as a semipermeable membrane for electrodialysis, reverse osmosis, and ultrafiltration.\(^4\) More recently, usage in gas separations has emerged.\(^5\) Specifically, membranes based on PBIs appear suitable for \( \text{H}_2 \) separation from \( \text{CO}_2 \) at high temperatures.\(^6\)–\(^8\)

The high rigidity and resistance to aggressive environments exhibited by PBIs originate from the close chain-packing imposed by strong, interchain hydrogen-bonding interactions,\(^9\) as well as from the presence of rigid aromatic rings which frustrate chain rotation. A further, very promising application of PBI is as a proton-exchange membrane for fuel cells (PEMFC). There is a need to introduce new materials capable of operating above 100 °C, thereby eliminating most of the severe limitations of conventional Naion membranes. In fact, in the range of 150–200 °C, these high-temperature PEMFCs exhibit such features as increased CO tolerance, increased electrocatalytic activity, simplified water management, and relaxed requirements for temperature control. PBI is the most widely used material for HT-PEMFC owing to its thermal and mechanical stability, low gas permeability, and tolerance to strong acids and CO. To improve proton conductivity, PBI is used in the doped form with appropriate levels of phosphoric acid.\(^2,11,12\)

PBI absorbs conspicuous amounts of water (around 15% by weight in ambient conditions). In such amounts, water can swell the polymer, perturb its H-bonding network, and bind preferentially onto interaction and/or free-volume sites that would be otherwise available for gas sorption and diffusion.\(^1,14\) Furthermore, plasticization by absorbed water adversely affects mechanical performance: both the compressive strength and dynamic modulus of wet PBI are approximately halved.
compared to the fully dried material, which may cause the premature failure of items exposed to humid environments.\textsuperscript{14} For example, these effects are to be carefully considered in applications involving membranes that operate with humidified gas streams. Despite the numerous studies already published on the subject, the molecular mechanism of water diffusion in PBI is still poorly understood. Thus, issues such as preferential interaction sites on the polymer substrate, type, and strength of probe/substrate H bonding; influence of PBI/H\textsubscript{2}O interactions on PBI self-interactions; and structural effects remain to be elucidated. In fact, conflicting and/or incomplete accounts on these and related matters have been reported.

Numerous experimental approaches have been employed to investigate water/polymer systems [solid-state NMR, Raman, Fourier-transform infrared spectroscopy (FTIR), neutron scattering, and light scattering] with varying degrees of success.\textsuperscript{15–18} To date, FTIR spectroscopy is considered among the most powerful and reliable techniques. This is due to its sensitivity toward H bonding and to its sampling flexibility, which allows one to implement in situ, time-resolved experiments in a rather straightforward way.\textsuperscript{16,19–21} However, problems are encountered even for this type of spectroscopy, mainly related to the considerable band broadening in the analytical range, which limits and often prevents the resolution of the multicomponent profiles. This effect is a direct consequence of H-bonding interactions and their wide distribution of geometrical parameters. Another limitation of the infrared technique results from intensity enhancement of \(\nu(\text{OH})\) bands upon the establishment of an interaction, which is directly related to H-bonding strength. This effect is difficult to predict and poses serious problems to the quantitative analysis.\textsuperscript{16,19,20}

Earlier contributions on FTIR spectroscopy of PBI tentatively identified spectroscopic signatures of free- and self-associated NH groups,\textsuperscript{22–24} which were later employed to investigate H bonding in the polymer as a function of doping,\textsuperscript{15,25–27} blend composition,\textsuperscript{16,23,28,29} and temperature.\textsuperscript{22,24,26} Bouchet and Siebert\textsuperscript{25} examined the FTIR spectrum of pristine and partially deuterated PBI. They confirmed previous assignments and, on this basis, attempted a quantitative interpretation of the vibrational bandshape observed in samples doped with HBr, H\textsubscript{2}SO\textsubscript{4}, and H\textsubscript{3}PO\textsubscript{4}. Because of the lack of resolution and the multiplicity of components, their attempts achieved limited success. Combining FTIR and solid-state NMR measurements, Brooks and coworkers\textsuperscript{14} concluded that FTIR results were unable to demonstrate conclusively the occurrence of strong intramolecular H bonding in the dry state being disrupted in the wet state. On the other hand, based on NMR results, they claimed that the majority of water in PBI is effectively mobile (in the time scale of the experiment) and therefore not bonded to the polymer. These authors attributed the loss in mechanical properties in wet PBI to the reduction in van der Waals forces and/or hydrogen bonding interactions between chains as a consequence of the swelling of the wet material. Leal and coworkers\textsuperscript{30} examined by FTIR spectroscopy the H-bonding formation in hydroxylated PBI fibers as a function of heat treatment. They identified bands associated with H bonding, measured their molar absorptivities, and quantified the concentration of N–H groups H-bonded to water and to adjacent polymer chains in the fiber. The above authors concluded that sorbed water strongly interacts with polymer N–H groups. More recently, Christensen and Jones\textsuperscript{31} investigated undoped PBI films as a function of humidity using both H\textsubscript{2}O and D\textsubscript{2}O in an attempt to deepen the understanding of the vibrational spectrum. These authors, in contrast with the conclusions of Brooks et al., claimed that H\textsubscript{2}O uptake by PBI results in the formation of regions of “free” water as well as the disruption of N–H···N interactions because of the insertion of water between PBI chains, which tightly bind to the active sites of the polymer.

In the present contribution, time-resolved FTIR measurements have been performed at two different relative pressures of water vapor to monitor H\textsubscript{2}O sorption in PBI. The evolution of the spectrum in the \(\nu(\text{NH})/\nu(\text{OH})\) range provided information about the molecular mechanism of diffusion and, together with in situ temperature measurements in the range 50–450 °C, contributed to clarify aspects of the vibrational interpretation which needed to be consolidated.

The spectral data have been analyzed by different and complementary approaches, namely, difference spectroscopy, two-dimensional correlation spectroscopy (2D-COS), and least-squares curve fitting (LSCF) analysis, which improved the resolution of the complex band profiles. The interpretation of the observed spectroscopic effects was made possible by comparison with the results of quantum chemistry (QC)/normal coordinate analysis (NCA). The first-principles simulation of the infrared spectra of simplified molecular models of PBI in the dry and hydrate forms was found in good agreement with the experimental results, confirming the predictive capabilities of the chosen model chemistry. Relevant structural information was also derived and discussed, which prompted future experimental activities.

2. RESULTS AND DISCUSSION

2.1. FTIR Spectroscopy. 2.1.1. Spectroscopic Monitoring of Sorption Kinetics. In Figure 1, the spectrum of a PBI film equilibrated under ambient conditions (red trace) and dried at 150 °C for 4 h (blue trace).

Figure 1. FTIR spectrum of PBI equilibrated at ambient conditions (red trace) and dried at 150 °C for 4 h (blue trace).
appreciated by difference spectroscopy. In Figure 2, the time evolution of the difference spectrum relative to the sorption experiment at \(p/p_0 = 0.1\) is reported.

![Figure 2. Evolution of the difference spectra as a function of time for the \(H_2O\) sorption experiment at 35 °C and \(p/p_0 = 0.1\).](image)

The \(\nu(OH)\) region displays both positive features because of the growing concentration of molecular species and a negative component (with respect to the local baseline, see Figure 2) related to an intensity reduction or a shift/widening of a PBI peak. Similar effects are observed in the bending and libration regions. Here, the PBI peaks are significantly sharper than the water bands and produce a series of derivative-type features characteristic of peak shifts. Overall, the sequence of difference spectra in Figure 2 demonstrates the sensitivity of the vibrational behavior of PBI to the presence of water. Because of the high sensitivity of difference spectra to peak shifts, these are difficult to interpret and use reliably for quantitative analysis.

However, one exception is found for the libration overtone at 2105 cm\(^{-1}\), which, as anticipated, is interference-free. A linear and reproducible baseline can be identified in all difference spectra (see inset of Figure 2), making it well-suited for concentration monitoring. The results gathered in this manner for two water sorption experiments carried out at 35 °C and at \(p/p_0 = 0.1\) and 0.5 (red and blue symbols, respectively) are represented in Figure 3A.

In Figure 3B,C, normalized absorbance is plotted against the square root of time. In the simplest case of water diffusion into a plane sheet exposed to constant vapor activity on both sides, Fick’s model can describe absorbance kinetics as:

\[
\frac{A(t)}{A_\infty} = \frac{M(t)}{M_\infty} = 1 - \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n + 1)^2} \exp\left[-\frac{D(2n + 1)^2\pi^2 t}{L^2}\right]
\]

where \(A(t)\) and \(A_\infty\) are the absorbance areas of the analytical band at time \(t\) and at equilibrium, respectively; \(M\) is the mass of sorbed penetrant; \(D\) is the mutual diffusivity; and \(L\) is the sample thickness. If the polymer undergoes additional relaxation during mass uptake, the Berens–Hopfenberg model can provide a more accurate fit.

![Figure 3.](image)

(A) Water vapor sorption kinetics as monitored by the \(H_2O\) band at 2105 cm\(^{-1}\). \(H_2O\) relative pressures as indicated. (B) Normalized absorbance vs square root of time at \(p/p_0 = 0.1\). (C) Normalized absorbance vs square root of time at \(p/p_0 = 0.5\). Continuous black curves represent the regression of the data with eq 3.
where \( A_{\infty,0} \) is the absorbance associated with the unrelaxed polymer, \( A_{\infty,1} \) is the absorbance associated with relaxation (\( A_{\infty,1} = A_{\infty} - A_{\infty,0} \)) and \( k_1 \) is a relaxation rate constant (s\(^{-1}\)). This model can be adjusted to control the changing water vapor concentrations at the film surface when initially exposed to vapor\(^{39}\)

\[
\frac{A(t)}{A_{\infty}} = \frac{M_t}{M_{\infty}} = \frac{A_{\infty,0}}{A_{\infty}} \left[ 1 - \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp \left( \frac{-D(2n+1)^2 \pi^2 t}{L^2} \right) \right] + \frac{A_{\infty,1}}{A_{\infty}} \left[ 1 - \exp(-k_1 t) \right]
\]

(2)

where \( \beta \) is a rate constant describing the initial change in surface vapor concentration upon water vapor exposure (s\(^{-1}\)).

The continuous lines in Figure 3B,C represent the least-squares regression of data points to the modified form of the Berens–Hopfenberg model (eq 3), where \( A_{\infty,0}, D, k_1, \) and \( \beta \) are used as fitting parameters.

A deviation of the experimental data from Fickian behavior is observed at \( p/p_0 = 0.1 \) at longer times, and this behavior becomes more apparent at \( p/p_0 = 0.5 \). This behavior appears to originate from a slowly increasing regime, following the initial steep water uptake, which prevents equilibrium attainment in the explored time range. Measurements at longer sorption times (\( \geq 50,000 \) s) indicated that, at \( p/p_0 = 0.5 \), the water uptake still continues at a barely detectable rate. This effect could be associated to slow relaxation processes in the polymer and is able to be adequately described by the modified Berens–Hopfenberg model. From least-squares regression, the diffusion coefficients of water at \( p/p_0 = 0.1 \) and 0.5 were determined to be \( 1.9 \times 10^{-9} \) and \( 2.7 \times 10^{-9} \) cm\(^2\)/s, respectively.

To avoid the complicating factors affecting the difference spectra, we turned our attention to the absorbance spectra. Their evolution during the sorption experiment at \( p/p_0 = 0.1 \) is depicted in Figure 4, showing a gradual increase of the main band at 3170 cm\(^{-1}\) and the occurrence of an absorption at 3620 cm\(^{-1}\), which is absent in the spectrum of the dry sample. The latter has already been mentioned in previous literature studies.\(^{13,14}\)

To provide a deeper analysis of this complex bandshape, we used 2D-COS, an approach that was found very effective for studying H-bonding systems.\(^{31,37–39}\) This method enhances spectral resolution and is valuable in cases of broad, highly overlapped profiles. The resolution enhancement originates from the spectral data spreading over a second frequency axis, coupled with the asynchronous correlation intensity vanishing for signals evolving at the same rate.\(^{37,38}\) The analysis produces two correlation maps: a synchronous spectrum that represents the simultaneous or coincidental changes of two separate signals and an asynchronous spectrum that highlights features evolving at significantly different rates. A feature specifically relevant in the present context is the synchronous spectrum along the main diagonal, often referred to as the power spectrum. It represents the autocorrelation function: the magnitude of the peaks in this pattern (autopeaks) is representative of the overall extent of intensity change occurring at the respective frequency. Thus, any region of a spectrum changing to a great extent will show strong autocorrelation peaks, whereas the regions remaining nearly constant will display weak or no autopeaks. The synchronous map relative to the sorption experiment at \( p/p_0 = 0.1 \) is reported in Figure 5A, whereas Figure 5B depicts the power spectrum in comparison with the frequency spectrum collected at 435 s.

Three maxima are identified in the synchronous map, which resolves the region between 3750 and 3480 cm\(^{-1}\) in two separate components at 3626 and 3505 cm\(^{-1}\). Below 3450 cm\(^{-1}\), the power spectrum displays a single feature centered at 3194 cm\(^{-1}\), whereas in correspondence to the peak observed at 3418 cm\(^{-1}\) in the frequency spectrum and to the shoulder at around 2800 cm\(^{-1}\), the autocorrelation intensity goes to zero. This is an indication that the above features remain essentially constant during the sorption process, their apparent changes being due to the influence of the intense, unresolved component at 3194 cm\(^{-1}\) which increases to a large extent (see Figure 4). The asynchronous spectrum is more complex and more difficult to interpret possibly because of its higher sensitivity to complicating factors such as peak shifts (vide infra). It is reported in Figure S2 of the Supporting Information. The main additional information it conveys is related to the resolution of two components evolving at different rates, centered, respectively, at 3110 and 3305 cm\(^{-1}\). These correspond to the maximum and the shoulder observed in the main band of the power spectrum.

In light of the 2D-COS results, it is possible to attempt a LSCF analysis of the experimental profiles. These can be suitably simulated by a model comprising five components.
(three, in the case of the dry sample) whose position can be identified by visual inspection (abrupt change of slope in the bandshape) as well as by the second-derivative analysis. Details on the adopted LSCF method are reported in the Supporting Information. The band at 3062 cm\(^{-1}\) is not considered in the analysis, being associated to the aromatic \(\nu (CH)\) modes that are invariant and unrelated to the interacting moieties. Typical LSCF results, relative to the spectra collected at 0 and 435 s, are represented in Figure 6A,B. The model reproduces satisfactorily the complex experimental profile, and the quality of the fit is consistent throughout the whole sequence of spectra (correlation coefficient, \(R^2 \geq 0.996\)). In Figure 7A,B are reported the band intensities of the five resolved components as a function of sorption time, that is, as a function of water concentration in the sample. The intensity parameter in Figure 7A is expressed in terms of percentage increase \([i.e., \text{as } 100 \cdot \left( A_t - A_0 \right) / A_0]\) to remove the molar absorptivity differences between the components. The two peaks at higher frequency for which \(A_0 = 0\) are monitored in terms of absolute absorbance (Figure 7B). The band originally centered at

**Figure 5.** (A) Synchronous map in the 2400—4000 cm\(^{-1}\) range for the sequence of spectra collected in the sorption experiment at 35 °C and \(p/p_0 = 0.1\). (B) Comparison between the autocorrelation spectrum from the synchronous map of (A) (red trace) and the frequency spectrum collected at \(t = 435\) s (blue trace).

**Figure 6.** (A) LSCF analysis of the spectrum collected at time = 0 s. The red trace is the experimental profile, the blue trace is the regression result, and the black traces are the three resolved components. (B) Same as (A) for the spectrum collected at 435 s. The experimental band is represented after the removal of the 3062 cm\(^{-1}\) component to demonstrate the actual simulated profile.

**Figure 7.** (A) Absorbance increase (%) for the components at 3167, 2860, and 3424 cm\(^{-1}\) as a function of sorption time. Frequency values are relative to the spectrum at 0 s. (B) Absorbance area of the components at 3628 and 3550 cm\(^{-1}\) as a function of sorption time. Frequency values are relative to the spectrum collected at 435 s. (C) Peak position of the component at 3424 cm\(^{-1}\) as a function of sorption time. All data refer to the experiment at 35 °C and \(p/p_0 = 0.1\). Continuous lines are for eye guidance.
3167 cm$^{-1}$ (in the following, band positions refer to the dry sample) is the component growing to the larger extent (around 160%), suggesting that the most penetrant molecules absorb strongly at this frequency. The band at 2860 cm$^{-1}$ remains essentially constant, whereas the peak at 3424 cm$^{-1}$ decreases slightly (less than 10%), nearly within the uncertainty limits of the LSCF analysis. The above findings are in full agreement with the 2D-COS results. Both components at 3628 and 3550 cm$^{-1}$ increase gradually, with the high-frequency band growing at a faster rate and to a slightly larger extent. This result suggests that the two signals originate from distinct H$_2$O species rather than from splitting of a single stretching mode induced by mechanical coupling.

Figure 7C presents the position of the PBI peak, originally centered at 3424 cm$^{-1}$, as a function of sorption time. The gradual red shift exactly matching the kinetics of the sorption process is to be interpreted, taking into account the invariance of the integrated intensity, that is, the concentration of the vibrating group. The shift is likely associated with a mean-field effect, that is, a change of the dielectric constant of the medium as a consequence of water uptake, which is described by the Kirkwood–Bauer–Magat (KBM) relationship.40 The observed red shift also accounts for the sharp relative minimum in the difference spectra (see Figure 2), to be associated predominantly to a first-derivative feature which resembles a negative peak because it is convoluted with a much broader and complex band profile. Band broadening may also play a role.

The significant perturbation of the PBI spectrum below 2000 cm$^{-1}$ in the presence of H$_2$O, evident in the form of multiple first-derivative features in the difference spectra (see Figure 2), is to be at least partially ascribed to the KBM effect rather than to the influence of specific molecular interactions on the vibrational behavior of the polymer.

2.1.2. Temperature Measurements. Further details on the complex interactional scenario were gained by performing in situ temperature measurement. In Figure 8A is reported the band profile in the 4000−2470 cm$^{-1}$ range (the interval where the spectrum changes most) at different temperatures from 50 to 450 °C. The experiment was carried out on a film equilibrated at ambient conditions containing 15 wt % of sorbed water. Sorbed water is still present up to 100 °C, indicated by the peak at 3620 cm$^{-1}$. At 150 °C and above, no spectral features related to sorbed H$_2$O are apparent. The total absorbance area is reported as a function of temperature in Figure 8B. The initial steep decrease is related to the loss of residual water. At 150 °C and above, the absorbance decrease becomes highly linear ($R^2 = 0.9965$), resembling the typical behavior of IR band intensities as a function of temperature. The spectra of Figure 8A collected in the range 200−450 °C were subjected to the LSCF analysis. A model comprising three Gaussian components was adopted, analogous to that used for the dry spectrum at room temperature, and the peak positions were allowed to vary in a narrow, predefined range to account for a possible frequency-to-temperature dependence.

The spectra of Figure 8A collected in the range 200−450 °C were subjected to the LSCF analysis. A model comprising three Gaussian components was adopted, analogous to that used for the dry spectrum at room temperature, and the peak positions were allowed to vary in a narrow, predefined range to account for a possible frequency-to-temperature dependence. As for the case of water absorption, all experimental profiles

Figure 8. (A) FTIR spectra of PBI collected at increasing temperatures in the frequency range 4000−2470 cm$^{-1}$. From top to bottom traces, $T = 100, 150, 200, 275, 350, 400, and 450 ^\circ C$. The arrow indicates the direction of temperature increase. (B) Total absorbance area (3800−2470 cm$^{-1}$) as a function of temperature. The inset highlights the 150−450 °C range.

Figure 9. Absorbance areas vs temperature for the three components obtained by LSCF analysis of the PBI spectrum in the 3800−2470 cm$^{-1}$ range. (A) Peak at 3424 cm$^{-1}$; (B) band at 3177 cm$^{-1}$; and (C) band at 2860 cm$^{-1}$.

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were satisfactorily simulated, with $R^2$ values always exceeding 0.996. Typical examples of the LSCF results for spectra collected at different temperatures are reported in Figure S3 of the Supporting Information. The absorbance area of the three resolved components are plotted as a function of temperature in Figure 9A−C. Although the two bands at 3177 and 2860 cm$^{-1}$ display a pronounced linear decrease, the peak at 3424 cm$^{-1}$ remains constant. This result resembles that obtained for the same peak at the increasing water content (see Figure 7A). Interestingly, all of the three components exhibit a departure from the respective linear behavior at temperatures above 400 °C. In particular, the band 3177 cm$^{-1}$ deviates below the extrapolated values, whereas the 3424 cm$^{-1}$ peak shows an opposite trend; the band at 2860 cm$^{-1}$ seems to remain constant above 400 °C. The region where the departures from linearity are observed exactly coincides with the glass transition temperature of PBI, reported in the literature (425 °C).$^{1,2}$

2.2. Interpretation of Spectra via QC/NC Analysis.

2.2.1. Dry Model. The theoretical calculation of the PBI vibrational spectrum requires a molecular model capable of capturing both the geometry (G matrix) and the electron density distribution (F matrix) of the system under scrutiny. At the same time, there is a need to restrict the problem to a manageable size, especially when dealing with computationally intensive calculations such as those required for evaluating infrared intensities. An additional problem arises when the investigated polymer is capable of self-association via H bonding. This kind of molecular interaction is known to influence the vibrational spectrum extensively and, therefore, needs to be properly simulated.$^{31,42}$ On these premises, we selected N-phenyl benzimidazole (Ph-BZI) as a model compound for the polymer chain. We were particularly interested in interpreting the $\nu$(NH)/$\nu$(OH) region, and the selected structural unit is believed to mimic accurately the behavior of the proton-donor/proton-acceptor system and its neighboring environment both in terms of steric hindrance and electronic distribution. The Ph-BZI molecule optimized by the adopted MM force field is planar with $C_{1h}$ symmetry; however, frequency analysis demonstrates that, at the density functional theory (DFT) level, the planar configuration is a saddle point, which can be crossed by inspection of the relevant degree of freedom. A slightly tilted geometry is a true stationary state (the angle between the phenyl and the benzimidazole ring, $\theta$, is 6.4°, which removes any symmetry). A conformational analysis along the relevant dihedral (results reported in Figure S4, Supporting Information) reveals the presence of a rather flat minimum at coplanarity ($\theta = 0^\circ$) encompassing a ±10° range, followed by a deep potential energy barrier ($\Delta E = 3.2$ kcal/mol). This indicates that, on forming supramolecular aggregates, the two ring system can be distorted only slightly from coplanarity to accommodate steric and/or interaction requirements.

From the vibrational standpoint, as expected, a single Ph-BZI molecule is an unrealistic model because it does not account for H bonding. A preliminary frequency calculation on the DFT-relaxed structure evidenced a reasonable agreement in the region below 1700 cm$^{-1}$ but inadequate correlation in the region between 4000 and 3000 cm$^{-1}$. The basic model compound was therefore made of two Ph-BZI units interacting via a N−H···N H bonding, as depicted in Scheme 1:

A critical problem for structure optimization at the DFT level, particularly relevant for supramolecular aggregates, is the choice of the starting-point geometry because the optimizing algorithm will invariably localize the minimum that is closer to the initial input. To address this issue, a preliminary MM analysis was performed, based on a Metropolis-Monte Carlo method specifically developed to investigate H-bonding complexes.$^{43,44}$ Details on the adopted computational approach are reported in the Supporting Information (see Figure S5). The minimum identified by the MM analysis was employed as the initial input for the structure relaxation at the DFT level, with no geometric constraints to the planarity of the single Ph-BZI substructures. The resulting supramolecular aggregate, represented in Scheme 1, was subjected to frequency analysis. Positive values for the whole set of calculated frequencies demonstrated the identified structure to be a true energy minimum, which is a prerequisite for the subsequent NCA.$^{45}$

The formation of a N−H···N interaction is witnessed by the geometrical parameters, force constant values, and vibrational frequencies of the groups involved (collected in Table 1), which conform to the general H-bonding formation criteria. In particular, a comparison between the values of the unperturbed proton donor [N34−H41, (NH)$_a$] and the bound NH group [N9−H16, (NH)$_b$] affords an estimation of the interaction strength. Thus, the N9−H16 bond length increases by 1.60% as a consequence of the proton-acceptor attraction, whereas the N−H force constant decreases by 9.92% as a result of the redistribution of the electron density. The H-bonding length is less than 2 Å, and the estimated binding energy ($E_b$) is 7.9 kcal/mol. All of the above parameters are characteristics of a strong interaction.$^{41,46,47}$

The conformational analysis and the geometry of the relaxed structure show that the two bulky Ph-BZI groups pose strict constraints on the spatial arrangements that the two substructures can assume for letting the molecular interaction to occur. In fact, to avoid close contacts, the two molecular planes are placed almost perpendicular to each other. A comparison between the calculated and experimental spectra in the frequency range 4000−2200 cm$^{-1}$ is presented in Figure 10, where the insets represent the forms of the two $\nu$(NH) normal modes. The $\nu$(NH)$_a$ vibration occurs at 3525 cm$^{-1}$, whereas the mode relative to the (NH)$_b$ group is located at 3248 cm$^{-1}$, that is, it is red-shifted by 277 cm$^{-1}$. Shifts toward lower frequencies are a common place for proton
Table 1. Relevant Parameters for the Bound and Free N–H Groups in the Dimeric Structure Optimized at the B3LYP/6-31G(d) Level of Theory

|            | Length (Å) | H-bond length (Å) | \( F_i \) (mdyne/Å) | \( \nu_{calc} \) (cm\(^{-1}\)) | IR intensity (km/mol) | \( E_0 \) (kcal/mol) |
|------------|------------|-------------------|---------------------|-----------------------------|-----------------------|---------------------|
| (N–H)\(_b\) | 1.025      | 1.988             | 6.685               | 3248                        | 921.9                 | 7.9                 |
| (N–H)\(_f\) | 1.009      | 7.420             |                     |                             |                       |                     |

Figure 10. Comparison between the experimental spectrum of dry PBI (150 °C, 5 h) in the \( \nu\)(NH) region and the calculated spectrum of the dimeric structure represented in Scheme 1. The insets are the displacement-vector representations of the two calculated \( \nu\)(NH) modes.

The intense and well-resolved absorption observed at 3420 cm\(^{-1}\) (3424 cm\(^{-1}\) after deconvolution) in the \( \nu\)(NH) region and the calculated spectrum of the dimeric structure represented in Scheme 1. The intensity and well-resolved absorption observed at 3420 cm\(^{-1}\) (3424 cm\(^{-1}\) after deconvolution) has been traditionally associated with the \( \nu\)(NH)\(_f\) vibration and would decrease to a large extent, following the sorption kinetics, rather than remaining constant (Figure 7A). (iv) The spectrum of pure benzimidazole in an argon matrix at 87 K displays a sharp peak at 3509 cm\(^{-1}\),\(^{31}\) which, because of the extreme dilution, corresponds to the \( \nu\)(NH) vibration in isolated, gaslike molecules. The calculated frequency has an \( \Delta\nu\) of 16 cm\(^{-1}\) with respect to the above value (a remarkable 0.4%), thus suggesting that, in the experimental PBI spectrum, the \( \nu\)(NH)\(_f\) vibration is not the prominent component at 3420 cm\(^{-1}\) but occurs with a barely detectable intensity just above 3500 cm\(^{-1}\). It is possibly associated with the bump observed in the 3800–3520 cm\(^{-1}\) range.

To conclude the analysis of the X–H range, the aromatic \( \nu\)CH stretchings produce a set of 18 closely lying frequencies which merge, upon correcting for finite bandwidth, in a single peak at 3089 cm\(^{-1}\). Both the position and the relative intensity of this feature compare well with the observed absorption at 3062 cm\(^{-1}\) (\( \Delta\nu\) = 24 cm\(^{-1}\), re = 0.8%), thus confirming its purely \( \nu\)(CH) character.

The correspondence between the calculated and the experimental spectrum is satisfactory also in the 1800–500 cm\(^{-1}\) interval (data reported in Figure S6, Supporting Information). A detailed interpretation of the whole spectrum is beyond the scope of the present investigation and will be the subject of a forthcoming study. An overall discussion of the main features, along with the most significant assignments, is reported in the Supporting Information.

2.2.2. Hydrate Models. The next step of our analysis is the simulation of the PBI spectrum upon \( \text{H}_2\text{O} \) sorption. First, hydrating model constructed by adding two water molecules to the DFT-relaxed structure of the dimer, interacting with the available H-bonding sites (respectively, N7 as a proton acceptor and N34–H41 as a proton donor; see atom numbering in Scheme 1). This arrangement corresponds to a situation, whereby the network of self-associated PBI units is not perturbed by the incoming \( \text{H}_2\text{O} \) molecules, which bind preferentially to the terminals of the H-bonding chains. Furthermore, the hydration process is limited to the saturation of interacting sites of the polymer substrate, neglecting the possible self-association of penetrant molecules (which will be considered afterward).

The starting-point geometry to be optimized by the chosen model chemistry was obtained by positioning the two \( \text{H}_2\text{O} \) probes in the regions of maximum likelihood occurrence for the specific donor–acceptor pairs, as identified by the IsoStar structural database (Cambridge Structural Database and PDB).\(^{52–54}\) Details of the procedure are reported in the Supporting Information. Figure 11 shows the calculated spectrum in the \( \nu\)(NH)/\( \nu\)(OH) range for the supramolecular aggregate of Scheme 2, along with the experimental spectrum of dry PBI. The insets represent the form of the three prominent normal modes.

The simulated spectrum resembles more closely the observed features in comparison with the dry model. Although...
the components at 3090 and 3192 cm\(^{-1}\) are only marginally affected, a doublet occurs at 3371 and 3366 cm\(^{-1}\) that merges to a single peak at 3370 cm\(^{-1}\) on correcting for a finite bandwidth. The position of this feature nicely correlates with the peak observed at 3420 cm\(^{-1}\) (fd = 50 cm\(^{-1}\), re = 1.5%), and the intensity is also reasonably reproduced. The two components at 3371 and 3366 cm\(^{-1}\) correspond, respectively, to the \(\nu\) (OH) of the water molecule interacting with the N7 nitrogen and to the N34–H41 stretching (see insets of Figure 11 and Tables 2 and 3). In this light, it is tempting to assign the 3420 cm\(^{-1}\) peak to a first-shell hydration layer, whereby the observed feature is originated by water molecules tightly bound to the available H-bonding sites on the polymer substrate, which cannot be eliminated at the drying temperature (150 °C). In this hypothesis, water sorption would occur by self-association of the incoming penetrant in successive hydration layers, which would produce signals similar to those of the liquid water, as it is actually observed. This interpretation, although reasonable, is ruled out by the high-temperature measurements previously discussed. It is unrealistic to assume that this first-shell layer may persist at temperatures up to 400 °C, where the intensity of the 3420 cm\(^{-1}\) peak remains invariant (see Figure 9A).

As a second hydrate model, we considered the case of water self-association, that is, when a second hydration shell adds on after (or concurrently with) the saturation of the H-bonding sites of the polymer substrate. To simulate this aggregate, we started with the relaxed structure of the hydrated dimer (Scheme 2), adding two water molecules in a position suitable for self-association to occur. Consideration was made of the preferential role that the two PBI-bound probes would play in self-association (i.e., proton donors are more likely to act as acceptors in a further H bonding and vice-versa), although the opposite mechanism cannot be entirely ruled out. Scheme 3 is to be considered as a likely structure within a complex distribution of geometries, which reflects itself in the breadth of the corresponding band. Once again, the starting position of the two H\(_2\)O molecules was set on the basis of the maximum likelihood occurrence, as per the IsoStar structural database (details in the Supporting Information).

The DFT-relaxed structure is reported in Scheme 3. Also, in this case, no imaginary values were found in the set of computed vibrational frequencies, confirming the nature of true energy minimum for the identified stationary point. It is found that all of the interactions retain a significant degree of directionality, especially those formed between N7 and the H\(_2\)O molecules denoted 1 and 3. The geometric parameters characteristic of the H-bonding interactions are reported in Table 4 along with force constants and calculated frequencies of the proton-donor bonds. In Table 5 are collected the vibrational parameters for the NH/OH normal modes. It is found that the N–H···N interaction is scarcely affected by self-association, as the NH length, the H-bonding length, and the frequency remain essentially constant and the IR intensity decreases by a factor of 0.7, whereas more pronounced effects are observed on the \(\nu\) (OH) modes. In particular, the vibration denoted \(\nu_{bN(H_2O)2}\) corresponding to the OH stretching of the water molecule bound to the N7 atom, displays a red shift of \(-219\) cm\(^{-1}\) and a 3.6-fold increase in intensity with respect to the same mode in the absence of self-association. This conspicuous effect is essentially electronic, resulting from the lowering of the OH force constant when the oxygen atom gets involved in a second interaction (\(F_I\) goes from 7.28 to 6.97 mdyne/Å, \(-4.3\%\), in passing from the isolated to the self-associated situation). The \(\nu_{bN(H_2O)2}\) mode becomes the prominent peak in the explored frequency range and nicely correlates with the experimental observation that water sorption produces a principal component centered at around 3170 cm\(^{-1}\) (see Figures 6 and 7A). Overall, the correspondence between the calculated and the experimental spectra, reproduced in Figure 12, is very satisfactory and significantly better than that achieved with the first hydrate model (compare Figures 11 and 12). The \(f_d\) between the main calculated component and the observed maximum is 6 cm\(^{-1}\)
whereas a closely lying relative-maximum observed at 3175 cm$^{-1}$ might be associated with the two $\nu$(NH) modes (see Table 5), providing an $f_d$ value of 15 cm$^{-1}$ and an $r_e$ of 0.5%. In this light, the band at 3175 cm$^{-1}$ which increases strongly on water sorption is to be mainly associated to the first hydration layer and, in particular, to the H$_2$O molecules interacting with the N proton acceptors. However, the position and the intensity of the band are characteristic of a self-associated species, which confirms the extensive clustering of the penetrant molecules. The doublet calculated at 3374–3344 cm$^{-1}$ originates, respectively, from the (H$_2$O)$_3$ and (H$_2$O)$_2$ molecules (see Table 5), hence from both the first and second hydration layers. This doublet cannot be associated to the peak observed at 3420 cm$^{-1}$ because the latter persists in the dry sample and is insensitive to water content (see Figure 7A). Thus, the two calculated components likely merge in the broad H$_2$O band observed at 3170 cm$^{-1}$. The five components calculated at above 3500 cm$^{-1}$, upon correcting for finite bandwidth, merge in two well-resolved bands centered at 3670 and 3545 cm$^{-1}$, respectively. These correlate satisfactorily with the features observed at 3628 cm$^{-1}$ ($f_d = 42$ cm$^{-1}$, $r_e = 1.1\%$) and 3536 cm$^{-1}$ ($f_d = 6$ cm$^{-1}$, $r_e = 0.3\%$) which, according to the above assignments, appear only upon water sorption. Thus, the 3670 cm$^{-1}$ band has a multicomponent character and originates from the whole set of H$_2$O molecules (see Table 4). It is not specific of a distinct hydration layer and/or an interaction site.

Conversely, the 3536 cm$^{-1}$ band is associated with a single vibration $[\nu_4$(H$_2$O)$_4]$; the diverse nature of the two bands (multicomponent vs single vibrational mode) accounts for their different kinetic behavior observed in the sorption experiment, whereby the multicomponent band increases at a faster rate and to a larger extent (see Figure 7B).

The vibrational analysis discussed above also affords an insight into the analytical potential of FTIR spectroscopy and, in particular, in the possibility of quantifying the different water species present in the system besides the overall amount of sorbed water. In fact, the development of predictive models for simulating diffusion behavior relies heavily on the knowledge of first-shell and second-shell population. Quantiﬁcation in the $\nu$(NH)/$\nu$(OH) range is to be performed by LSCF resolution, which has been demonstrated to be highly reliable.
Table 4. H-Bonding Parameters (Proton-Donor Length, H-Bonding Length, Force Constant, and Calculated Frequency) for the Five Interactions Formed in the Second Hydrate Model (Scheme 3) Optimized at the B3LYP/6-31g(d) Level of Theory

| X-H length (Å) | H-bonding length (Å) | F_s(μN/m) (dyn/cm) | ν(X-H) (cm⁻¹) |
|----------------|----------------------|---------------------|----------------|
| N-H            | 1.028                | 1.958               | 6.530          | 3191          |
| H-O-H-N        | 0.996                | 1.808               | 6.973          | 3153          |
| H-O-H          | 0.985                | 1.833               | 7.274          | 3374          |
| H-O-N          | 1.028                | 1.815               | 6.750          | 3213          |
| H-O-H          | 0.987                | 1.799               | 7.215          | 3344          |

“The relevant proton donor is highlighted in column 1.

Table 5. Calculated IR Parameters (Frequency, Intensity, and PED) and Description of the X–H (OH/NH) Normal Modes for the Second Hydrate Model (Scheme 3) Optimized at the B3LYP/6-31g(d) Level of Theory

| frequency (cm⁻¹) | IR intensity (km/mol) | PED (%) | description |
|------------------|-----------------------|---------|-------------|
| 3672             | 99.1                  | 80 T₂   | ν_s(H₂O)   |
| 3669             | 60.2                  | 98 Q₂   | ν_s(H₂O)   |
| 3653             | 33.5                  | 95 S₂   | ν_s(H₂O)   |
| 3641             | 47.4                  | 92 R₂   | ν_s(H₂O)   |
| 3545             | 140.4                 | 80 T₂, 19 T₁ | ν_s(H₂O) |
| 3374             | 362.8                 | 92 S₁   | ν_b(H₂O)₁ |
| 3344             | 479.1                 | 91 Q₁   | ν_b(H₂O)₁ |
| 3213             | 302.6                 | 88 U    | ν_b(N≡N–H4I) |
| 3191             | 861.7                 | 86 W    | ν_b(N–N–H16) |
| 3153             | 1974.5                | 87 R₁   | ν_b(H₂O)₂ |

“Q₁ = str(O52–H51); Q₂ = str(O52–H53); R₁ = str(O55–H56); S₁ = str(O61–H66); S₂ = str(O61–H62); T₁ = str(O58–H57); T₂ = str(O58–H59); U = str(N34–H41); and W = str(N9–H16). The above internal coordinates are identified in Scheme 3. For complete atom numbering, refer to Figure S9 of the Supporting Information. Subscript meaning: as = antisymmetric; s = symmetric; f = free; b = bound; bO = bound to oxygen; and bN = bound to nitrogen.

Figure 12. Comparison between the experimental spectrum of PBI exposed to H₂O vapor for 435 s (p/p₀ = 0.1) and the calculated spectrum of the hydrate model represented in Scheme 3.

Of the five resolved components, the main band at around 3170 cm⁻¹ comprises contributions from first-shell water [ν_bN(H₂O)₂, ν_bO(H₂O)₁] and from a second-shell species [ν_bN(H₂O)₂, ν_bN(H₂O)₁]. In the absence of interference, considering that ν_bN(H₂O)₂ and ν_bN(H₂O)₁ vibrations display close intensity values (calculated I_bN/H2O = 1.3 ± 1, see Table S5) and that the ν_bO(H₂O)₁ mode is largely prevalent with respect to ν_bN(H₂O)₁ (calculated I_bN/H2O = 4.1 ± 4, see Table S5), the absorbance–concentration relationship would read

\[ \frac{A_{3170}}{L} = \frac{A_{3170}}{A_{3170}} \equiv \varepsilon_{bN}[C_2 + 0.2(C_1 + C_3)] \]

In eq 4, ε_bN refers to the molar absorptivity of the ν_bN(H₂O)₂ mode. Thus, the thickness-normalized absorbance of the 3170 cm⁻¹ band, A_{3170} would be proportional to C₂ with minor contributions from C₁ and C₃; these contributions cannot be separated. A further problem in this frequency range is the occurrence of the two ν(NH) modes and, particularly, the ν(N9–H16) vibration, whose intensity is comparable to that of the ν_bN(H₂O)₁ mode (calculated intensity ratio = 0.44). ν(NH) intensity cannot be considered a constant contribution of the polymer substrate to be subtracted out; in fact, the vibrational analysis demonstrates that I for the two above modes changes to a large extent upon the establishment of the molecular interaction with water (compare respective values in Tables 1 and 5). In summary, the 3170 cm⁻¹ band, despite its intensity, does not possess the required specificity to be used for concentration monitoring.

As already noted, the band at 3670 cm⁻¹ includes all four H₂O species. The components at 3641 cm⁻¹ [ν_b(H₂O)₂], 3653 cm⁻¹ [ν_a(H₂O)₂], and 3669 cm⁻¹ [ν_a(H₂O)₁] have comparable intensities (average value, \( \bar{I} = 47.0 \) km/mol; std = 13.3 km/mol), whereas the component at 3672 cm⁻¹ [ν_a(H₂O)₁] is significantly stronger (\( I_{3672}/\bar{I} = 2.1 \approx 2 \)). The monocomponent peak at 3545 cm⁻¹ is slightly more intense than its counterpart at 3672 cm⁻¹ (\( I_{3545}/I_{3672} = 1.4, I_{3545}/\bar{I} = 3 \)). Rearranging the relevant absorbance–concentration relationships and making use of the mass balance, we can write

\[ \frac{A_{3670} – 0.33\varepsilon_{3545}}{L} = \bar{F} \cdot C_{tot} \]

Equation 5 (details of derivation in Supporting Information, p. 21–22) affords the evaluation of \( \bar{F} \) by coupling spectroscopic observables (\( \bar{A}_{3670}, \varepsilon_{3545} \)) with gravimetric data (\( C_{tot} \)) collected in the same conditions. In turn, \( \bar{F} \) provides an estimate of the different water species according to \( C_{tot} \).
Returning to the predictive performances of the various models, it is concluded that the hydration model accounting for self-association is largely improved with respect to the model with only PBI/H2O interactions and provides reliable assignments for most of the features observed in the IR spectrum. The only peak yet to be assigned is the one at 3420 cm⁻¹, for which none of the explored models is capable of providing a calculated frequency with which it can be associated.

Combining the experimental and computational evidence gathered herein, we conclude that the above feature is due to a paracrystalline domain present in the polymer bulk and developed during the film-forming process from the N,N-dimethylacetamide (DMAc) solution. PBI is generally regarded as a fully amorphous material on the basis of its wide-angle x-ray scattering (WAXS) pattern (see Figure 13). It displays a complex amorphous-like halo which can be resolved with at least two main components at 2θ = 15° and 23°. A third, low-intensity peak, much sharper than the main components is identified at 2θ = 18°. Some authors interpreted this feature in terms of an incipient-ordered structure; they note that its intensity depends on the preparation protocol and can be enhanced by appropriate high-temperature treatments. A patent has been issued in which the authors describe a process for increasing the crystallinity of PBI fibers by contacting them at elevated temperature with suitable solvents.

The concept of PBI crystallinity is, therefore, not new, but no specific signatures in the infrared spectrum have been associated so far with an ordered phase.

The WAXS pattern of amorphous polymers displaying two distinct components has been associated to the occurrence of two characteristic interchain spacings in the disordered phase. The considerably larger breadth of these components with respect to those of a crystalline phase is related to the wider distribution of spacing in the amorphous domains. An analogous situation is realized in the infrared spectrum. Here, the interchain spacing manifests itself in the position and breadth of the ν(NH) bands; in fact, shorter interchain distances correspond to closer donor--acceptor positions which, in turn, are reflected in stronger H-bonding interactions and lower absorption frequencies. The FWHH is related to the distance distribution. Following the same line of reasoning, the peak at 3420 cm⁻¹ is ascribed to a distinct phase characterized by a sharper distribution of chain distances and hence a greater degree of order with respect to the amorphous phase. In this intermediate mesophase, the interchain distance is constant and larger than that in the amorphous domains, as suggested by the higher frequency maximum (3420 vs 3165/2862 cm⁻¹). This interpretation also accounts for the trend of the band intensities as a function of temperature (Figure 9A–C). For the two amorphous components, the absorbance area decreases linearly up to 400 °C. This behavior is generally a combination of two effects, namely, the dependence of molar absorptivity with temperature (linear decrease) and the lowering concentration of H-bonded species as temperature increases. In the present case, the first effect is likely prevailing because we do not observe a concurrent absorbance enhancement due to newly formed, free NH groups. The change of slope at around 420 °C is related to the T_g of the material. Because of the increased molecular mobility, H-bonding interactions in the amorphous phase start to dissociate, and the intensity of the band decreases below the value predicted by a pure absorptivity-temperature effect. Concurrently, we observe an increase in band intensity at 3420 cm⁻¹ which remained constant up to the T_g suggesting that a fraction of the amorphous phase is transformed into the partially ordered mesophase by an annealing process. The present results suggest that heat treatments above 450 °C in inert atmosphere may impact on the permselectivity properties of PBI membranes. In situ experiments in this temperature range and selective deuteration experiments at low D2O activities are currently underway to confirm the above conclusions and obtain further structural information.

3. CONCLUDING REMARKS

In this article, the infrared spectrum of PBI in the dry and hydrate forms has been investigated to gain a deeper interpretation of its complex features. In particular, the object of study was the ν(NH)/ν(OH) range which is extensively affected by sorbed water. Coupling experimental measurements (isothermal H2O sorption and in situ temperature measurements) with first-principles theoretical calculations allowed us to obtain satisfactory assignment of the main spectral features and relevant structural information.

The principal conclusions of the present study can be summarized as follows:

- In the dry form, the complex ν(NH) bandshape originates from the extensive NH–N self-association, coupled with the presence of distinct structural features. In particular, the two-component character of the main ν(NH) band parallels the previously reported WAXS pattern and has been attributed to the occurrence of two distinct amorphous regions with characteristic average spacing.
- A further, much sharper component at higher frequency has been tentatively assigned to a partially ordered mesophase, whose amount is found to increase at the expense of the amorphous content at temperatures higher than 400 °C, that is, above the T_g of PBI. The latter assignment disproves previous literature interpretation.
- Sorbed water displays a principal component at 3175 cm⁻¹ and two bands at higher frequency which were
assigned on the basis of QC/NC analysis. The first-principle calculations provided good agreement with the experimental data and represented an essential tool for interpreting the vibrational behavior of this complex system.

- Theoretical evaluation of absolute intensities for the various υ(OH) components allowed us to identify bands that can be directly correlated with gravimetric data for calibration purposes, providing a means to measure the absolute concentration of specific H₂O species.

4. EXPERIMENTAL SECTION

4.1. Materials. Celazole S26 solution was purchased from PBI Performance Products Inc. This solution contains 26% of solid PBI dissolved in DMAc with 1.5 wt% LiCl added to enhance the polymer solubility. The molecular formula of PBI is reported in Figure S1 of the Supporting Information. DMAc was purchased from Sigma-Aldrich and used without further purification. Celazole films were cast after diluting the PBI solution to 2 wt% polymer by adding DMAc and stirring overnight. The solution was filtered using a 0.45 μm PTFE filter and sonicated for 30 min to remove any bubbles. The solution was poured onto a glass plate and placed in a vacuum oven on a level surface. The solvent was removed by drying for at least 24 h under vacuum at room temperature, followed by 4 h at 80 °C and 1 h at 100 °C. After the film was removed from the glass plate, it was boiled in deionized (DI) water for 4 h to remove residual DMAc. The film was then soaked in DI water at room temperature for at least 24 h to ensure complete removal of LiCl. Finally, the film (thickness = 10.8 μm) was dried under vacuum at 140 °C for 24 h. Thermogravimetric analysis and FTIR confirmed complete solvent removal.

4.2. FTIR Spectroscopy. A custom-designed, vacuum-tight FTIR cell was used to acquire time-resolved FTIR spectra during sorption experiments. Spectral data were collected in the transmission mode on the polymer film exposed to water vapor at a constant relative pressure (i.e., ratio of the pressure of pure water to the vapor pressure of water at the test temperature, p/p₀). The cell, equipped with ZnSe windows, was accommodated in the sample compartment of a suitably modified FTIR spectrometer. It was directly connected through service lines to a water reservoir, a turbo-molecular vacuum pump, a pressure transducer [MKS Baratron 121 (Andover, MA); full scale, 100 Torr; resolution, 0.01 Torr; accuracy, ±0.5% of the reading], and a Pirani vacuumometer. Full details of the experimental setup are reported elsewhere. Before each sorption measurement, the sample was dried under vacuum at 150 °C for 4 h in the same apparatus used for the test. Drying in situ is essential in the present experimental procedure because the thin PBI film absorbs water almost instantaneously when exposed to the atmosphere. The FTIR spectrometer was a Spectrum 100 from PerkinElmer (Norwalk, CT) equipped with a Ge/KBr beam splitter and a wide-band deuterated triglycine sulfate detector. The transmission spectra were collected with the following instrumental parameters: resolution = 2 cm⁻¹; optical path difference velocity = 0.5 cm/s; and spectral range = 4000–500 cm⁻¹. Spectra were acquired in the single-beam mode using a dedicated software package for time-resolved spectroscopy (Timebase from PerkinElmer).

Absorbance spectra were obtained using a background collected on the cell with no sample inside at the test conditions (i.e., at the same relative pressure of water vapor used for the sorption measurement). Difference spectra were obtained as Aₛ = Aᵣ − k·Aᵥ, where A is the absorbance, and the subscripts d, s, and r denote, respectively, the difference spectrum, the sample spectrum ("wet" specimen), and the reference spectrum ("dry" specimen). k is an adjustable parameter which allows compensation for thickness differences (if any) between the sample and the reference spectra. It was experimentally verified that negligible changes in thickness take place during the sorption measurement at p/p₀ = 0.1; therefore, the k values were consistently taken as unity. FTIR transmission spectra in the temperature range 35–450 °C were collected in a HT/HP cell (GS05850 from Specac Ltd., Orpington, UK) coupled to a GX spectrometer (PerkinElmer). The cell operates in the 30–450 °C range at up to 10 000 psi. The measurements were performed in an inert atmosphere (a continuous flux of dry N₂) on a PBI film equilibrated under atmospheric conditions. Resolution of multicomponent bands into individual peaks was achieved by an LSCF algorithm based on the Levenberg–Marquardt method. Details on the adopted models and the regression method are reported in the Supporting Information.

4.3. Computational Methods. All of the molecular mechanics (MM) calculations were performed using the MMFF92 force field (Merck Molecular Force Field, from Merck Co, Kenilworth, NJ, USA), optimized for organic compounds. The potential energy surface of the model compounds was explored by a Metropolis-Monte Carlo method for systematic variations of the distances/angles in a predefined supramolecular assembly. Details of the adopted approach are reported in the Supporting Information.

QC calculations were performed using unrestricted DFT. In particular, the hybrid method referred to as B3LYP was used, in combination with the standard 6-31G(d) basis set. This method includes the Becke’s three-parameter exchange functional coupled with the Lee–Yang–Parr correlation functional.

The binding energy of the dry model, Eᵣᵣ, was calculated in the frame of the supermolecule method, as the energy difference between the complex and the sum of the isolated monomers, each relaxed to their minimum energy configuration. By adopting this definition, negative energies favor the aggregate formation. Eᵣᵣ was corrected for the basis set superposition errors (BSSE), which is generally non-negligible for H-bonding complexes. BSSE was calculated using the counterpoise method of Boys and Bernardi. For complexes with multiple interactions, Eᵣᵣ was not evaluated because of the ambiguity introduced when separating different contributions.

After geometry optimization, a NCA at the same level of theory was performed, comprising the calculation of the Hessian matrix (F) by analytical evaluation of the first and second derivatives of the potential energy with respect to the...
Cartesian displacement coordinates. The \( F \) matrix was then transformed in terms of mass-weighed coordinates and diagonalized to obtain the corresponding eigenvalues (normal frequencies) and eigenvectors (displacement vectors, \( \mathbf{L} \) matrix). Finally, transformation into a set of nonredundant internal coordinates of both the \( \mathbf{F} \) and \( \mathbf{L} \) matrices was accomplished to express the force constants in structurally meaningful terms and for characterizing the normal modes in terms of their PED, which is expressed, in the normalized form, as:

\[
(PED)_{jk} = \frac{F_{jk}^2}{\sum F_{ij}^2} \times 100
\]

In eq 6, PED is the percent contribution of the \( j \)th internal coordinate to the \( k \)th normal mode, \( F_{jk} \) is the \( j \)th diagonal Force constant, and \( L_{jk} \) is the corresponding element of the \( \mathbf{L} \) matrix. Only the diagonal terms of the \( \mathbf{F} \) matrix were considered. DFT and NCA calculations were performed by the Gaussian 03 program package (Gaussian Inc., Pittsburgh, PA), and the results were visualized with the associated GaussView graphic interface. PED calculations were carried out with the aid of the VEDA program.

ASSOCIATED CONTENT

Supporting Information

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Notes

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