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Unique Orientation of the Solid−Solid Interface at the Janus Particle Boundary Induced by Ionic Liquids

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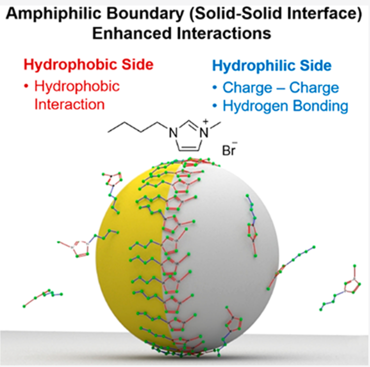
ABSTRACT: This study reveals the unique role on Janus particles of the solid−solid interface at the boundary in determining particle interactions and assembly. In an aqueous ionic liquid (IL) solution, Janus spheres adopt intriguing orientations with their boundaries pinned on the glass substrate. It was further discovered that the orientation was affected by the particle amphiphilicity as well as the chemical structure and concentration of the IL. Further characterization suggests that the adsorption on the hydrophilic side is due to both an electrostatic interaction and hydrogen bonding, while adsorption on the hydrophobic side is due to hydrophobic attraction. Through the concerted interplay of all these interactions, the amphiphilic boundary may attract an excessive amount of IL cations, which guide the unique orientations of the Janus spheres. The results highlight the importance of the Janus boundary that has not been recognized previously. Adsorption at the solid−solid interfaces may inspire new applications in areas such as separation and catalysis.



Janus particles assemble into remarkable superstructures due to different chemical makeups and properties on the two sides of a single particle.[1−5] The anisotropy of the particles enables directional interactions that lead to well-defined assembly structures, where the particle orientation is a key feature.[6,7] The orientation of Janus particles may also lead to novel applications that would be nearly impossible to achieve with homogeneous particles. For example, dipolar Janus particles have been controlled with external electric fields, and their orientational change could be used as a switch for e-paper displays.[8] Recently, the orientation of Janus particles at the liquid−air interface was utilized for surface functionalization and coating applications.[9,10] In previous studies, we showed that amphiphilic Janus spheres orient with their hydrophobic sides toward each other due to the attractive hydrophobic interactions in aqueous suspensions.[11] We further demonstrated that the assembly of these particles in the presence of small surface-active molecules is more complicated and governed by a balance of interactions, including electrostatic, hydrophobic, and van der Waals forces.[12] In this study, we investigate the influence of ionic liquids (ILs), which can be viewed as a special class of surfactants with unique molecular geometry and active surface properties.[13,14] The imidazolium cation examined here has a significant tendency to self-aggregate due to the delocalized positive charge within the imidazolium ring and the ubiquitous hydrogen bonds among the cations.[15,16]

Surprisingly, most of the Janus spheres "stand" directly at their boundaries when adsorbed onto the glass substrate in dilute aqueous solutions of ILs, in contrast with their more random orientation in deionized water (DIW) (Scheme 1a and b). This intriguing orientation associated with the solid−solid interface at the Janus boundary has not been observed in bulk solutions before. Studies investigating the importance of the Janus particle boundary mainly involve particles adsorbing at an interface or active self-propelling particles.[17,18] The only comparable investigation is in a simulation study, where the nonhomogeneous ion distribution was shown near the metal−dielectric Janus particle surface, which promotes the formation of a positively charged ring in the presence of multivalent ions.[19] Our results highlight a previously unrecognized aspect of the Janus particle boundary through experiments: the unique solid−solid nature of its interface.

In the literature, a solid−solid interface is usually created by the grain boundaries on solid materials between different crystalline structures or crystalline−amorphous phases.[20,21] Most such solid−solid interfaces are not amphiphilic, unlike the ones created by amphiphilic Janus spheres. It is well-known that amphiphilic molecules will preferentially adsorb at the liquid−liquid interface or the liquid−air interface to lower the free energy of the system.[22−24] However, the study of adsorption on a solid−solid interface is much more challenging. One report created a solid−solid interface using

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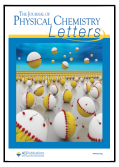
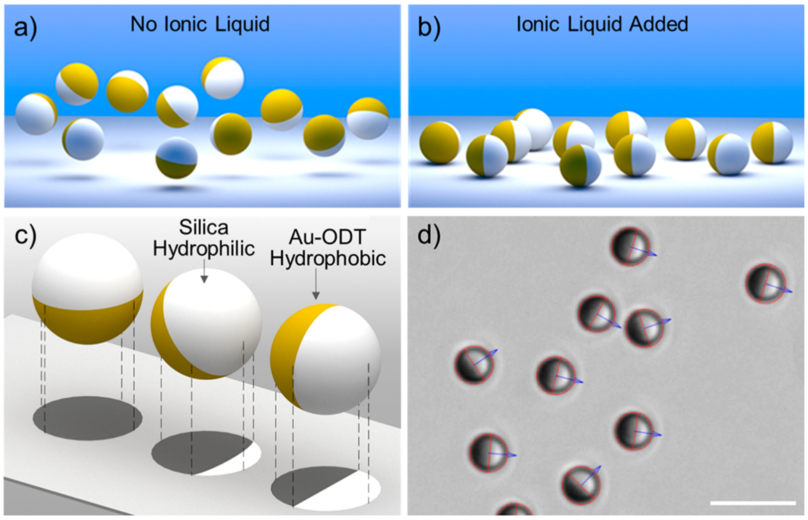
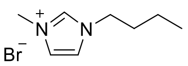
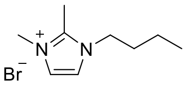
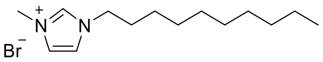


Scheme 1. (a) Sedimentation of Janus Particles Dispersed in DIW, (b) Janus Particles Assembled after Adding the IL, (c) 2D Projections of Janus Particles, and (d) Particle Tracking and Orientation Analysis with a Matlab Code[a]



[a]The scale bar is 10 μm.

Table 1. Chemical Structures, Abbreviations, and Characteristics of ILs Examined in This Study

Ionic liquid	Abbreviation	Chemical structure	Mw (g/mol)	CMC (mM)
1-Butyl-3-methylimidazolium bromide	$[C_4mim^+][Br^-]$		219	Not forming micelle
1-Butyl-2,3-dimethylimidazolium bromide	$[C_4C_1mim^+][Br^-]$		233	Not forming micelle
1-Decyl-3-methylimidazolium bromide	$[C_{10}mim^+][Br^-]$		303	30-40

special nanophase-separated amphiphilic conetworks and demonstrated that proteins were enriched by up to two orders of magnitude in such a system.[25] The specialized fabrication and complicated morphology of amphiphilic solid networks make it difficult to probe the detailed interactions. In addition, the adsorption onto solid−solid interfaces is inevitably more complicated due to the involvement of three phases. In this study, the geometry of the Janus spheres provides a straightforward platform to represent the solid−solid interface with a well-controlled morphology and chemistry, which opens new opportunity for systematically examining the physical chemistry in detail. In addition, there are several other advantages of creating the solid−solid interface using Janus particles. The interface is visible for micrometer-sized Janus spheres under a microscope, and a relatively large amount of such interface can be generated with a batch of particles.

The amphiphilic Janus spheres were fabricated using a previously published method using a Au coating and a 1-octadecanethiol (ODT) modification[12,17] A monolayer of particles was formed above a flat substrate through a simple sedimentation. Negative charges on the silica side of the Janus particles provide repulsions against aggregation and keep particles mobile on the substrate (Scheme 1a). Under bright field microscopy, the black side on a Janus sphere corresponds to the Au-coated hydrophobic side (blocking the light transmission), while the bright side is the transparent uncoated hydrophilic silica. This contrast is then utilized to analyze the Janus sphere orientation. The 2D projections of Janus spheres vary from a completely dark circle to a half moon shape (Scheme 1c). A MATLAB code was developed to analyze the particle orientation and estimate the out-of-plane angle, θ, based on the ratio of bright and dark pixels of the 2D projection (Scheme 1d, see details in the Supporting

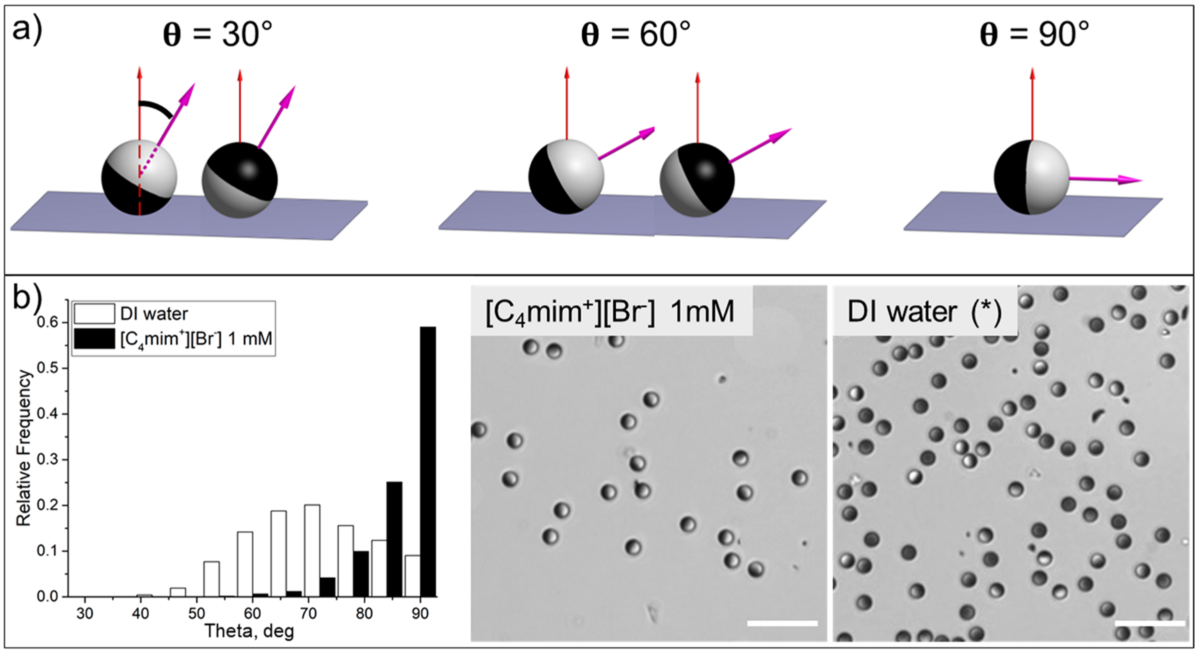


Figure 1. (a) Schematics of Janus particles oriented at 30°, 60°, and 90° θangles and (b) the orientation distribution of assembled Janus particles (the bin size is 6°) and corresponding optical images of ODT-modified Janus particles in a 1 mM aqueous solution of the [C_4mim$^+$][Br$^-$] IL and DIW, where (*) indicates that the particles are mobile. The scale bar is 15 μm.

Information). Our previous studies revealed that when counterions were introduced and screened the electrostatic repulsions, particles oriented with their hydrophobic Au sides toward each other (Figure S1a). Adding an anionic surfactant can modulate the assemblies, but the hydrophobic Au sides still prefer to orient toward each other (Figure S1b). On the other hand, adding a conventional cationic surfactant leads to chain-like assembly structures (Figure S1c). However, when an IL was introduced, these particles showed intriguing orientations (Scheme 1b and d). All the particles were pinned to the glass substrate exactly at the boundary on the Janus particles and stayed immobilized. To study the factors that may influence the unique orientation of Janus spheres, we synthesized several highly pure ILs with similar chemical structures (Table 1).

The compounds' purities and structures were confirmed with an NMR analysis (Figure S2). Changing one substituent group in the cation at a time allowed us to test the contribution of certain chemical structures. The 1-butyl-2,3-dimethylimidazolium bromide IL, [C_4C_1mim$^+$][Br$^-$], was synthesized to examine the role of an acidic C2 proton in the imidazolium cation, which has been shown to be a primary source of hydrogen bonding between the cation and anions.[26] The 1-decyl-3-methylimidazolium bromide IL featuring a decyl alkyl group, [C_{10}mim$^+$][Br$^-$], was used to test the effect of the hydrocarbon chain length and hydrophobic interactions.

To quantify the orientation distribution, we analyzed the out-of-plane angle, θ, for Janus particles at different experimental conditions. The definition for θ is the angle between the Janus particle's axis and the vector normal to a substrate, as outlined in Figure 1a. It should be noted that when using this method the estimation of the out-of-plane angle is the most accurate when θ is close to 90° but less precise when θ is small due to the low contrast between the two hemispheres. Therefore, we only presented an angle distribution in the range from 30° to 90°. In addition, we could not differentiate whether the Au side was oriented upward or downward from the images, although it is more probable for a particle to orient with the Au side downward due to the weight of a metallic cap and the repulsion of the silica side with the substrate.[27]

The orientation distribution clearly shows that Janus particles prefer to stand at the boundary when adsorbed onto the glass substrate in the presence of the [C_4mim$^+$][Br$^-$] IL at a concentration of 1 mM (Figure 1b). Both the hydrophilic side (bright) and the hydrophobic side (dark) can be equally visible under the microscope. More than 85% of Janus particles had a θ value higher than 80°. In addition, particles are immobilized on the substrate, which indicates a strong attraction. At an IL concentration of 0.5 mM, Janus particles stay mobile and do not get pinned to the substrate. Meanwhile at higher concentrations (2 mM and 5 mM), Janus particles are pinned at the Janus boundary with an orientation distribution similar to that of the 1 mM concentration (Figure S3). In a control experiment without the IL, Janus spheres dispersed in deionized water (DIW) oriented much more randomly and mostly appeared dark gray under the microscope (Figure 1b). Repulsion between negatively charged silica surfaces on the hydrophilic hemisphere of the Janus particles and the silica surface of the glass substrate keeps particles rotating slightly above the substrate. Although there is certain preference for orientation ~60−70°, mainly due to the uneven weight distribution induced by the Au coating and charge−charge interactions, there is no preference for orientation around 90°. Such an orientation behavior of the Janus particles in ionic solutions has not been observed previously. In addition, to the best of our knowledge, no current theory could be used to explain this intriguing phenomenon.

The amphiphilicity of Janus spheres is an important factor contributing to the particle orientation. We modified the Au side of the Janus particles with thiols of different lengths to probe the role of the hydrophobicity. Figure 2a shows that only

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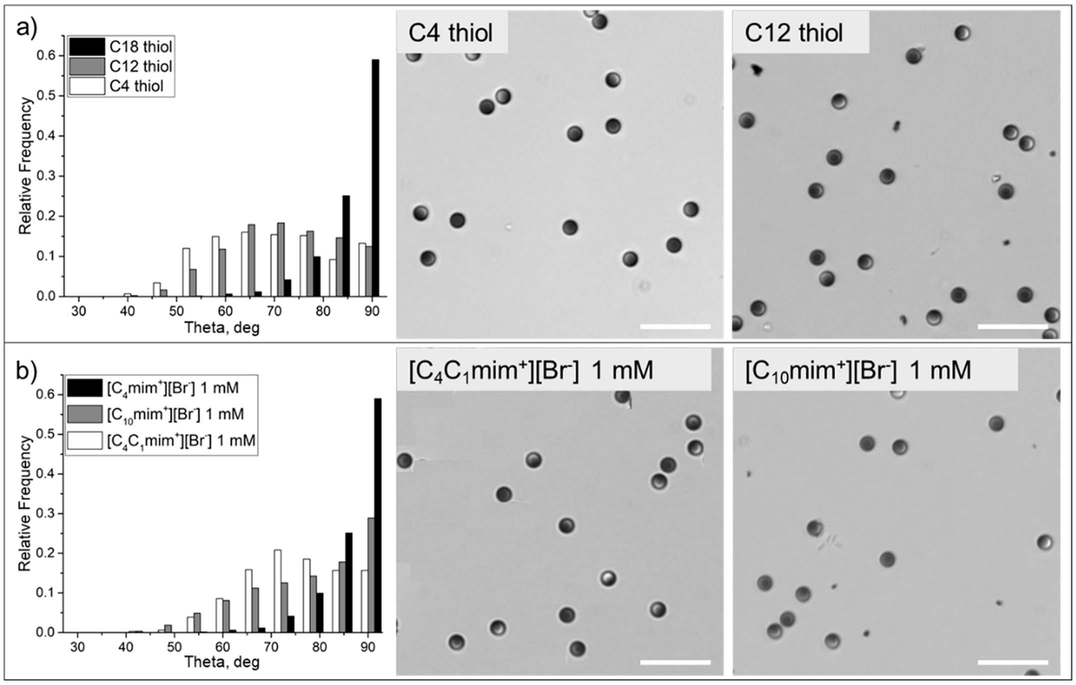


Figure 2. (a) Orientation distribution of Janus particles modified with different thiols at 1 mM $[C_4mim^+][Br^-]$ and corresponding optical images of Janus spheres modified with C4 and C12 thiols. (b) Orientation distribution of Janus particles under different ILs and corresponding optical images of Janus spheres in a 1 mM aqueous solution of methylated IL, $[C_4C_1mim^+][Br^-]$, and an IL possessing a long carbon alkyl chain substituent, $[C_{10}mim^+][Br^-]$. The scale bar is 15 μm.

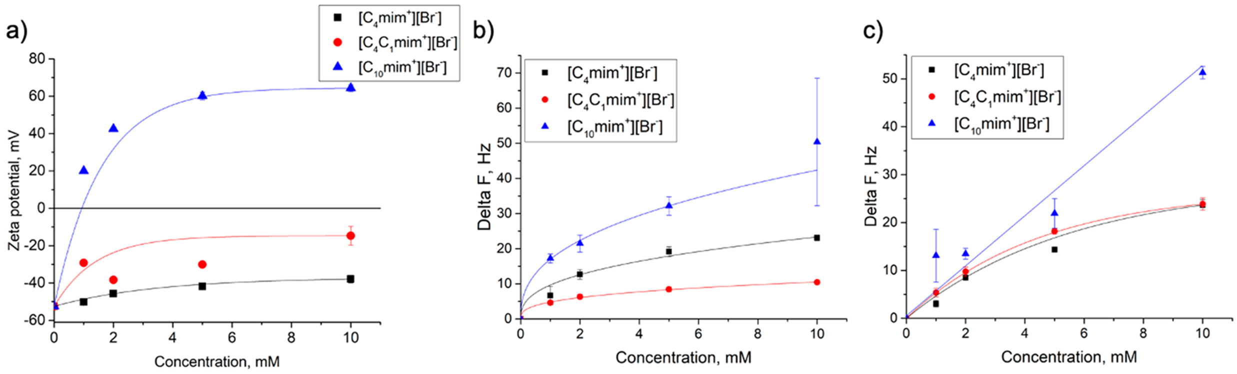
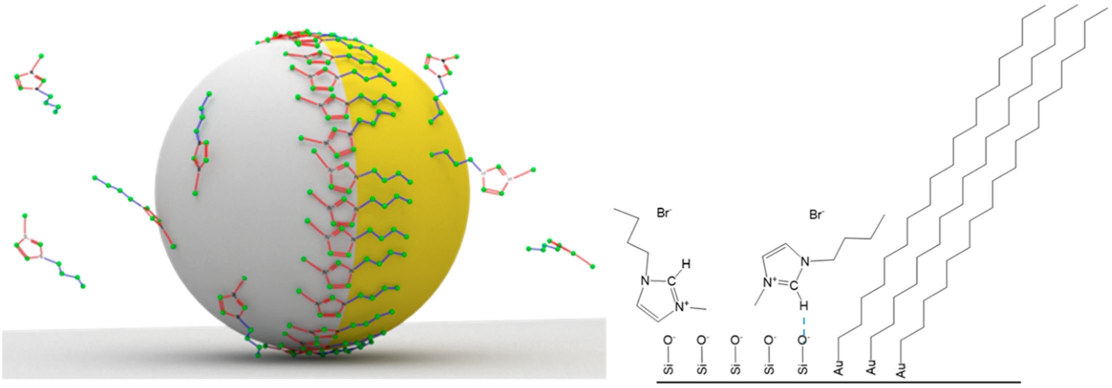


Figure 3. (a) ζ-Potential of silica particles in different IL solutions, (b) frequency change in the QCM measurement on a silica-coated substrate, and (c) frequency change in the QCM measurement on hydrophobic ODT-modified Au substrates.

22−26% of Janus particles with shorter thiol attachments were pinned at the Janus boundary, compared to ∼85% for Janus particles modified with the C18 thiol. The values of the θ distribution of Janus particles modified with C4 and C12 thiols is similar to that of particles dispersed in DI water due to weakened hydrophobic interactions. These results suggest that only the highly amphiphilic hydrophilic−hydrophobic boundary of the Janus particles could promote the unique orientation.

Structural features of the IL cation also contribute significantly to the particle orientation. Imidazolium-based ILs are known as silanol masking agents in reverse-phase high-performance liquid chromatography.[28] They have been used to shield residual silanol groups of a silica stationary phase via electrostatic and hydrogen bonding interactions. Previous studies also showed a strong interaction between the silica nanoparticles and the imidazolium-based ILs.[29] The same interactions could also be responsible for the nonequilibrium nature of the assembly. To verify the impact of hydrogen bonding, experiments were carried out with the $[C_4C_1mim^+]$-$[Br^-]$ IL. The methylation of the C2 atom of the imidazolium cation in $[C_4C_1mim^+][Br^-]$ (see Table 1) decreases its hydrogen bonding capability. It should be noted that the hydrophilic side of the Janus particles and the glass substrate are both made from silica surfaces. We observed no strong preference in the θ distribution for Janus particles in the presence of the $[C_4C_1mim^+][Br^-]$ IL (Figure 2b). This suggests that hydrogen bonding may play a role in the unique orientation of Janus particles. To further probe the interactions of ILs with the silica surface, we also examined the aggregation behaviors of fluorescently labeled homogeneous silica nanoparticles (100 nm) in the presence of an IL (Figure S4). These silica nanoparticles were well-dispersed in DIW without the ILs. Upon adding the $[C_1C_4mim^+][Br^-]$ IL, only a few clusters were observed. On the other hand, adding the nonmethylated IL analogue, $[C_4mim^+][Br^-]$, triggered the severe aggregation

Scheme 2. Schematic Plot of the Proposed Mechanism[a]



[a] The [C_4mim^+][Br^-] IL excessively adsorbs onto the silica−Au boundary of the amphiphilic Janus particle.

of the silica nanoparticles, and a network of large aggregates was observed. We believe this network of aggregates is the result of both electrostatic screening and hydrogen bonding bridged by the [C_4mim^+][Br^-] IL. These results confirm that hydrogen bonding is critical to the surface adsorption of the IL. It induces a strong attraction between the silica surfaces of the glass substrate and the silica side of the Janus particles. The adsorption of the IL on both Janus particles and substrate, and the subsequently induced attractions, lead to the pinning of the Janus particles to the substrate.

To test the role of the IL hydrophobicity, we examined the particle orientation with the [$C_{10}mim^+$][Br^-] IL. The θ distribution analysis showed that only ∼45% of Janus particles orient at a θ angle higher than 80°, compared to 85% for the [C_4mim^+][Br^-] IL (Figure 2b). The difference might be explained by the longer alkyl chain substituent within the [$C_{10}mim^+$][Br^-] IL forming a bilayer or semi-micelles on the silica side. The literature has shown that imidazolium-based ILs with an alkyl chain of eight carbon atoms or longer can form micelles.[30] We confirmed this by ζ-potential measurements, which indicated that the [$C_{10}mim^+$][Br^-] IL quickly reverses the negative charge of 500 nm silica particles to positive even at low concentrations (Figure 3a). However, [C_4mim^+][Br^-] does not reverse the negative charges on the silica particles.

Our results indicate that multiple interactions can contribute to the adsorption of ILs as follows: (1) a hydrophobic interaction between the hydrophobic tail of the IL and the hydrophobic thiol layer on the Au side of Janus spheres, (2) an electrostatic force between the positively charged cation of ILs and the negatively charged silanol groups on the silica side of particles and silanol groups of the glass substrate, and (3) hydrogen bonding between the acidic proton of the imidazolium cation and silanol groups of the silica surface. The detailed interactions of Janus spheres with the substrate can be rather complicated due to the adsorption of the IL. However, the preference for Janus spheres to orient with the boundary pinned on the substrate suggests that the adsorption of the IL at the boundary may be stronger than elsewhere on the particle.

Based on all these results, we propose a hypothesis based on the adsorption of ILs on the amphiphilic Janus particles (Scheme 2). ILs could adsorb in excess at the hydrophobic−hydrophilic solid−solid interface at the Janus boundary due to the concerted interplay of electrostatic, hydrogen bonding, and hydrophobic attractions. This accumulation of the IL at the Janus particle boundary may dominate the interactions between Janus particles with the substrate and pin the particles via electrostatic forces and hydrogen bonding. However, it is very challenging to directly measure the adsorption of the IL at the Janus boundary. Attempting to use a dye or a nanoparticle to label the interface may change the IL adsorption dynamics. Other characterization tools such as Raman spectroscopy currently do not have the sensitivity and resolution to detect concentration changes around the small local area around the boundary. To gain more understanding of IL adsorption on Janus spheres, we carefully measured the adsorption of the IL on both hydrophilic and hydrophobic surfaces, which provided further evidence to support our hypothesis.

A quartz crystal microbalance (QCM) was utilized to study the adsorption behavior of ILs. Measurements were performed on hydrophobic thiolated Au and a hydrophilic silica-coated crystal, mimicking the Au and silica sides of the Janus particle, respectively. QCM measures the changes in the resonance frequency of a piezoelectric crystal due to the adsorbate's mass. Panels b and c in Figures 3 indicate that [C_4mim^+][Br^-] adsorbs similarly onto the hydrophilic silica and the hydrophobic Au surfaces, respectively, in the 1−10 mM concentration range. The [$C_4C_1mim^+$][Br^-] IL adsorbs onto the hydrophobic crystal as much as the nonmethylated IL analogue (Figure 3c). Both ILs have a four carbon alkyl chain substituent, and similar adsorption values were expected. However, the [$C_4C_1mim^+$][Br^-] IL adsorbs less onto the silica coated crystal since it does not possess a strong hydrogen bonding character due to the blocked acidic proton. Adsorption values of the [$C_{10}mim^+$][Br^-] IL were higher than those of the other two ILs. Higher adsorption onto the thiolated Au can be explained by the stronger hydrophobic interaction of the longer decyl alkyl chain substituent. Higher adsorption values on the silica surface might be due to the formation of a bilayer. Imidazolium-based ILs with an alkyl chain of eight carbon atoms or longer are known to form micelles.[30] Although the critical micelle concentration (CMC) of [$C_{10}mim^+$][Br^-] is 20−40 mM, the molecules could form semi-micelle or bilayer structures at the liquid−solid interface range.[29,31−33] The adsorption data were also consistent with the ζ-potential measurement, which showed a charge reversal of the silica nanoparticles in a solution of [$C_{10}mim^+$][Br^-] at concentrations below the CMC (Figure 3a), which also suggests multilayer structures of ILs on the particles surface.

To further study interactions among silica surfaces in the IL solutions, we utilized AFM to measure the force profiles

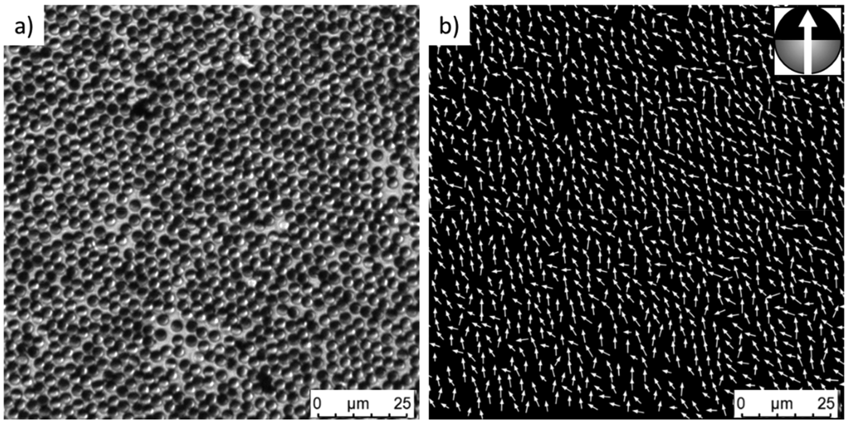


Figure 4. (a) Assembly of the Janus particle into 2D crystals in a 5 mM aqueous solution of $[C_4mim^+][Br^-]$ IL. (b) Tracking results of the particle orientations, where an arrow indicates an in-plane orientation of the Janus particle.

between a colloidal 5 um probe (glass bead) and a glass substrate in the wet samples. We then compared the values of the rupture forces. For a control sample with a colloidal probe immersed in DIW, the average rupture force was of 0.23 ± 0.16 nN (Figure S5). In a solution of the methylated $[C_4C_1mim^+][Br^-]$ IL, the average rupture force was around 0.34 ± 0.18 nN. In a solution of the $[C_4mim^+][Br^-]$ IL, which exhibits hydrogen bonding with the silanol groups of the silica, the average rupture force reached 0.43 ± 0.39 nN. These values are very noisy due to the challenges in measuring the force profiles in wet samples. Nonetheless, the higher adhesion between the probe and the substrate in the solution of $[C_4mim^+][Br^-]$ suggests that hydrogen bonding may lead to a higher adsorption of the IL and induce stronger attractions among the silica surfaces.[34]

When the particle concentration was high, a unique crystal structure of the Janus spheres emerged in the presence of ILs. In this experiment, the $[C_4mim^+][Br^-]$ IL solution was added to a high-concentration monolayer of Janus particles dispersed in DIW. A 2D crystal with striking orientation patterns was formed (Figure 4a). Most of the particles oriented on the Janus boundary similar to the dilute case. The in-plane orientation of the Janus particles is highlighted by symbolizing the orientation with an arrow pointing from hydrophilic side toward the hydrophobic side (Figure 4b). It is obvious that the in-plane orientation is highly correlated, similar to the crystal formed by dipoles.[35] The structures formed here may be due to the difference in the adsorption of the IL on the two sides of the Janus spheres, which may lead to dipole−dipole-like interactions. However, the details and mechanisms of the crystal structure formation are out of the scope of this report. It is also important to note here that since particles are pinned on the glass substrate, the orientation may not be thermodynamically equilibrated.

In conclusion, we demonstrate the unique orientations of amphiphilic Janus spheres, standing at their Janus boundaries, near a glass substrate in IL solutions. When formed into a 2D crystal, in-plane orientations of the Janus spheres in the assembled crystal structures are highly correlated. QCM, AFM, and ζ-potential measurements provide the details of the surface adsorption and interactions under IL adsorption. These results suggest that a combination of interactions is responsible for this unique behavior, including electrostatic forces, hydrophobic attractive forces, and hydrogen bonding. The $[C_4mim^+][Br^-]$ IL adsorbs on the silica side of the Janus spheres via hydrogen bonding and electrostatic attraction. On the other hand, the ILs also adsorb on the hydrophobic Au-coated side via hydrophobic attractions. The different adsorption mechanisms on the hydrophobic and hydrophilic hemispheres of the Janus particle may become additive at the amphiphilic boundary, which creates an even stronger adsorption of the IL at this solid−solid interface. Although the accumulation of amphiphilic molecules at the liquid−liquid or liquid−air interface has been extensively studied, the adsorption at the amphiphilic solid−solid interface is new. These intriguing orientations and assembly structures help draw the attention to the Janus boundary and highlight the importance of the solid−solid interface. The results here may inspire more studies to reveal the physical chemistry phenomena and other assembly structures featuring an amphiphilic boundary and interface. Furthermore, preferential adsorption may inspire new applications in separations and purification as well as catalysis, where surfaces are important in modulating molecular interactions.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpclett.0c02813.

Experimental details (materials, synthesis of ionic liquids, sample fabrication, AFM, and QCM), additional optical and fluorescent images not presented in the main text, NMR analysis results, and distribution of the rupture force (PDF)

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Notes

The authors declare no competing financial interest.

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