Stability and Exchange Processes in Ionic Liquid/Porphyrin Composite Films on Metal Surfaces

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Supporting Information

1. INTRODUCTION

One key ingredient for the development of high-performance, multicomponent, molecular thin-film devices is a molecular-level understanding of the adsorption and assembly of organic constituents on the solid substrate. Desired surface and interface arrangements and properties can only be achieved by deliberate choice of the involved molecular building blocks and control of the interplay between molecule–substrate and intermolecular interactions.1−10

Owing to their vital role in numerous biological catalytic reactions and transport processes,11,12 porphyrins are of particular interest for technical applications.5,7,9,13−17 They offer great functional diversity by variation of the substituents at the periphery of the tetrapyrrole core of the molecule. Knowledge and control of the formation and structure of self-assembled porphyrin adlayers on the surface of solid supports are essential for the synthesis of custom-tailored materials and catalysts.5,8,9,13,14,18 The preparation of catalytically active porphyrin-functionalized metal surfaces can be achieved by physical vapor deposition (PVD) in ultrahigh vacuum (UHV).5,9,15 One particularly popular and well-studied representative is 5,10,15,20-tetraphenylporphyrin (2H-TPP, see Figure 1a).

With reference to the rapidly growing interest in the development of organic−organic multicomponent heterostructures on metals,18,20−28 recent studies on porphyrins and related aromatic molecules highlight the importance of the strength of the organic−metal interaction and how it relates to the stability and arrangement of stacked multilayer architectures within organic bilayer structures on metals.5,6,29

Wang et al. studied the deposition of copper-phthalocyanine (Cu-Pc) onto monolayers of 6,13-pentacenequinone (P2O) or 5,7,12,14-pentacenethetone (P4O) on Ag(111) at room temperature (RT). They found that P2O is exchanged by Cu-Pc on the Ag(111) surface, whereas for P4O, no exchange occurs, that is, Cu-Pc remains on top of the P4O layer.27

Gallego et al.29 deposited a fullerene derivative (phenyl-C61-butryric acid methyl ester, PCBM) onto a layer of a TTF
derivative (2-[9-(1,3-dithiol-2-ylidene)anthracen-10(9H)-ylidene]-1,3-dithiole, exTTF) on Au(111). PCBM was found to replace a large fraction of the exTTF molecules from the metal surface to the outer surface because of preferential interaction with the gold substrate. This exchange does not occur, however, if the thickness of the exTTF layer is more than one monolayer.

Deimel et al. studied the deposition of ruthenium-tetraphenylporphyrin [Ru(CO)TPP] and iron-phthalocyanine (Fe-Pc) on a self-assembled monolayer (SAM) of 4-fluorothiophenol (4-FTP) on Ag(111) at 90 K. Upon heating the resulting Ru(CO)TPP/4-FTP/Ag(111) and Fe-Pc/4-FTP/Ag(111) systems, they observed by temperature-programmed X-ray photoelectron spectroscopy (XPS) that the Ru(CO)TPP and Fe-Pc molecules slip under the SAM at temperatures of 175 and 235 K, respectively. On the basis of earlier work, they concluded that the interaction of Fe-Pc with the silver substrate is comparatively stronger.

Interestingly, various other porphyrins deposited onto SAMs on Au, that is, 2H-TPP/C₈H₁₇SH (with 8–16 C atoms; SAM thickness: 1.25–2.13 nm), Co-TPP on 4-pyridinethiolate, and 2,3,7,8,12,13,17,18-octaethylporphinatozinc (Zn-OEP) on 4-pyridinethiolate, appeared to be stable at RT. In the latter two cases, the N atom of 4-pyridinethiolate binds to the respective central metal atom of Co-TPP and Zn-OEP.

Thussing and Jakob also observed temperature-dependent exchange processes while heating stacked layers of Cu-Pc and 3,4,9,10-perylene-tetracarboxylic-dianhydride (PTCDA) on Ag(111) deposited at 80 K. Notably, the thermal stability of the bilayer changes drastically if the order of the stack is reversed, which is related to the simultaneous desorption of molecules. Similar exchange and desorption phenomena were observed for bilayers of titanyl-phthalocyanine and PTCDA on Ag(111).

The aim of our study now is to study the interaction of adsorbed porphyrin monolayers with ionic liquids (ILs) and the stability of sequentially deposited composite layers under well-defined UHV conditions. As far as we are aware of, this is the first investigation of this kind. ILs are salts with a melting point typically below 100 °C, which combine extremely low vapor pressures with a large number of tunable chemical and physicochemical properties, depending on the nature of their cation/anion combination. In analogy to the above-mentioned examples, molecular exchange and preferential adsorption were also observed after sequential deposition of two different ILs on Ag(111). In particular, the selective replacement of anions and cations at the metal interface was found. After deposition below 90 K, the exchange occurs during heating at around 190 K. This temperature agrees well with the bulk glass transition temperature of the postdeposited IL.

Thin films of ILs are of high relevance for a variety of applications. Deposited on high surface area solid supports, they are the key ingredient to effective SCILL (solid catalyst with IL layer) and SILP (supported IL phase) catalysts.

2. EXPERIMENTAL SECTION

[Cr(C₈C₁Im)][PF₆] was purchased from Sigma-Aldrich (purity >95%), and 2H-TPP was purchased from Porphyrin Systems (purity 98%). Both chemicals were carefully degassed in UHV at an elevated temperature prior to the deposition experiments. [Cr(C₈C₁Im)][PF₆] and 2H-TPP were deposited via PVD using two separate effusion cells at temperatures of around 443 and 590 K, respectively. The flux was checked with a quartz crystal microbalance before and after deposition. With the exception of dialkylimidazolium halides, most other alkylimidazolium ILs evaporate intact in the form of neutral ion pairs.

Round Ag(111) and Au(111) single crystals with diameters of 15 mm were purchased from MaTeck (purity 99.9999%, polished with an alignment better than 0.1° to the (111) plane). The crystals were prepared by Ar⁺ sputtering (600 V, 8 μA, 30 min) followed by annealing (800 K, 10 min). The temperature of the single crystals was measured using type K thermocouples put into a 0.5 mm wide pinhole of the crystal with an absolute accuracy of ±20 K and a reproducibility of ±2 K.

The UHV system ARXPS has been described previously.

In short, the ARXP spectra were acquired using a non-monochromated Al Kα X-ray source (SPECXS XR 50, 1486.6 eV, 240 W) and a hemispherical electron analyzer (VG SCIENTA R3000). A pass energy of 100 eV was applied for all spectra yielding an overall energy resolution of about 0.9 eV. The spectra were quantitatively evaluated in CasaXPS V2.3.16Dev6. We subtracted Shirley backgrounds for Ag 3d and Au 4f core levels. Because of overlapping plasmon and shake-up satellites and the inelastically scattered electrons of the Ag 3d lines, an additional background was

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3. RESULTS AND DISCUSSION

3.1. Growth and Desorption of 2H-TPP on Ag(111) and Au(111). As a first step, we characterize the growth behavior of 2H-TPP on the two different substrates. For coverages of up to one closed layer of 2H-TPP, that is, for molecules in direct contact with the substrate, the behavior is well-studied on Ag(111) and Au(111). In contrast, information on the multilayer structure of porphyrins on metal substrates is scarce. For applications in organic electronic devices, this multilayer structure is of utmost importance because the molecular arrangement and orientation define parameters such as charge-carrier mobility and device efficiency.

To investigate the growth of 2H-TPP from sub-monolayer to multilayer coverages, we deposited increasing amounts of 2H-TPP onto the two substrates. Figure 2 shows the attenuation of the ARXPS signal intensity (at 0° and 80°) of the supporting metals (Ag 3d and Au 4f) as a function of porphyrin coverage on Ag(111) and Au(111), respectively, for deposition at RT (between 295 and 315 K) and at low temperature (LT, between 80 and 85 K). Overall, we observe very similar behavior on the two surfaces and at both temperatures. In each case, the data for 80° (open symbols) exactly follows the prediction for 2D growth (dashed lines; see the Experimental Section for details on the calculation) up to one monolayer, that is, an average thickness of ~0.34 nm. This behavior indicates the formation of a homogeneous closed layer of flat-lying porphyrin molecules, in line with the literature. Self-assembly of the porphyrin molecules into extended, ordered 2D networks on Ag(111) and Au(111) has been reported at RT and below 100 K. Isolated 2H-TPP molecules are considered highly mobile on both metal surfaces at 300 K, and the formation of ordered 2D networks is driven by the relatively strong molecule–molecule interaction.

The good agreement between the substrate signal intensity and the calculation for 2D growth continues until a coverage of approximately two monolayers (~0.68 nm) is reached. This behavior suggests that upon increasing the coverage, a second closed layer is formed on top of the first 2H-TPP layer. For higher coverages, the 80° data points in Figure 2 fall above the prediction for 2D growth (dashed lines), which is indicative of 3D island growth. This growth behavior is denoted as Stranski–Krastanov-like growth.
on top of two closed molecular layers was also observed for Cu-Pc on Cu(111) at RT\textsuperscript{129} and for other large \(\pi\)-conjugated molecules on Ag(111) and Au(111).\textsuperscript{141−144} While the initial 2D adlayers benefit from the strong adsorption of the molecules to the metal surface, the formation of relaxed 3D crystallites on top of the initial adlayers could be thermodynamically favored because it lowers the contact area to the strained layers below.\textsuperscript{142} From crystallography, tetragonal\textsuperscript{145} and triclinic\textsuperscript{146} structures were reported for 2H-TPP. Within the porphyrin crystals, the macrocycle is less twisted than in the surface-confined 2H-TPP monolayer on Ag(111) and Au(111); furthermore, in the crystal, stacking of the aromatic systems dominates the intermolecular interactions,\textsuperscript{145,146} whereas in the 2H-TPP monolayer on Ag(111) and Au(111), T-type interactions determine the structure.\textsuperscript{97,133,134,136} This results not only in different tilt angles of the phenyl legs with respect to the macrocycle but generally very different molecular arrangements.\textsuperscript{127}

Comparing the data at RT (red) to that at LT (blue) in Figure 2, we note that the variation of the support temperature between 80 and 315 K does not affect the growth behavior of 2H-TPP on both surfaces in the first two layers. In a previous study, Rojas et al.\textsuperscript{135} reported for 2H-TPP on Ag(111) at 58 K the nucleation of a second layer of porphyrin molecules on top of initial adislands before the completion of the first layer. While terrace diffusion on Ag(111) was reported to occur at temperatures as low as 58 K, the porphyrin islands of double-layer height appeared to be stabilized by limited diffusion of the molecules across the island boundaries. Upon heating above 100 K, the second-layer porphyrin molecules crossed the island boundaries and attached to the periphery of the first-layer islands.\textsuperscript{132} Our results indicate that immediately after impact on the surface at 80–85 K, the kinetic energy of the 2H-TPP molecules is large enough to enable diffusion across the island boundaries, allowing for the formation of flat 2D islands for coverages of up to two closed porphyrin layers on Ag(111) and Au(111).

Next, we address the thermal stability of 2H-TPP multilayers on Ag(111) and Au(111). Figure 3 shows the thermal evolution of the porphyrin C 1s and the corresponding metal substrate signals at 0° emission during heating of 2H-TPP multilayer films up to 540 K. The behavior on both surfaces is very similar. The signals remain constant until 440 K, where the C 1s intensity starts to decrease, and simultaneously the Ag 3d and Au 4f intensities increase. This behavior is attributed to desorption of the 2H-TPP multilayers, which is completed at around 480 K, above this temperature, no further changes are observed. From a Leading-Edge-like analysis\textsuperscript{107,147} of the data, we obtain an activation energy \(E_A\) of 193 kJ/mol (±22 kJ/mol) for multilayer desorption of 2H-TPP. From the residual C 1s intensity and the remaining attenuation of the Ag 3d and Au 4f substrate signals, we conclude that one closed monolayer of intact 2H-TPP remains present after multilayer desorption.

Our observations are in agreement with a previous temperature-programmed desorption study of 2H-TPP on Ag(111),\textsuperscript{122} where the multilayers were found to desorb below 490 K. Furthermore, previous studies demonstrated—in contrast to earlier assumptions\textsuperscript{9,122,123,127}—partial dehydrogenation of 2H-TPP monolayers on Ag(111) above 525 K.\textsuperscript{9,122,123} While the exact onset of decomposition is still not clear and no detailed study on Au(111) is available, we refrained from heating above 500 K during the preparation of a monolayer coverage of 2H-TPP by multilayer desorption to avoid any undesired reactions of the 2H-TPP molecules. Di Santo et al. reported a shift to lower BE of the N 1s and C 1s signals and a change in the C 1s peak shape after heating to 550 K in case of Ag(111); both effects were attributed to a change in the orientation of the phenyl groups of the 2H-TPP molecule relative to the metal surface upon dehydrogenation.\textsuperscript{123} In the present study, the spectra of monolayer 2H-TPP films showed no difference after heating to 500 K compared to films of similar thickness prepared by direct deposition.

### 3.2. Growth and Desorption of [C\textsubscript{6}C\textsubscript{1}Im][PF\textsubscript{6}] on 2H-TPP-Covered Ag(111) and Au(111)

To study the interaction between the IL [C\textsubscript{6}C\textsubscript{1}Im][PF\textsubscript{6}] and the neutral...
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2H-TPP molecule, we deposited [C8C1Im][PF6] onto Ag(111) and Au(111) covered with one closed monolayer of 2H-TPP (prepared by multilayer desorption at 480 K, see previous section). For comparison, we performed the same experiments also on bare surfaces. In each case, the IL growth behavior was monitored via the attenuation of the metal signals, I_d/I_0, as a function of the IL film thickness; note that for the 2H-TPP-precovered surface, I_0 is smaller than for the bare surface because of the attenuation by the preadsorbed porphyrin layer. Figure 4 shows the corresponding data for IL deposition at RT (green and red symbols) and at LT (blue; only for bare metal surfaces); the data for [C8C1Im][PF6] on bare Ag(111) was in part already published. For ILs, the coverage of 1 ML is defined as one layer ion pairs vertically arranged on top of each other, with a height 0.77 nm for [C8C1Im][PF6] thus, one closed layer of anions and cations adsorbed next to each other corresponds to 0.5 ML (for details, see the Experimental Section).

Up to a coverage of 0.5 ML [C8C1Im][PF6] (0.38 nm), the 80° data for both 2H-TPP-precovered surfaces in Figure 4 (open green symbols) display the characteristics of 2D growth, that is, they follow the dashed lines. This behavior indicates the formation of a homogeneous IL wetting layer (WL) with anions and cations adsorbed next to each other on top of the 2H-TPP monolayer. The formation of a WL is also observed for [C8C1Im][PF6] on bare metal surfaces (open red symbols). At IL film thicknesses above 0.5 ML, that is, starting with the second molecular IL layer, we systematically find a lower attenuation (larger intensity) in the 80° data than predicted for ideal 2D growth (dashed line). This deviation appears to be larger on the 2H-TPP-covered metals (green) than on the bare metals (red, blue) and indicates a more pronounced 3D character of the IL islands. The growth behavior of [C8C1Im][PF6] on the bare Ag(111) and Au(111) surfaces is very similar to each other and does not appear to be influenced by a variation of the support temperature between 80 and 315 K. For details on the molecular orientation for varying thicknesses of [C8C1Im][PF6] films on bare Ag(111) and Au(111) at RT, see Figure S1 in the Supporting Information.

Figure 5 shows the F 1s, N 1s, and C 1s spectra at 80° emission after deposition of 1.3 ML of [C8C1Im][PF6] on top of a monolayer of 2H-TPP on Ag(111) at RT. Notably, measurements at 80° (grazing emission) probe only the topmost surface layers. With an ID of only 1–1.5 nm, the resulting XP spectra are very sensitive to changes in the composition of the IL/vacuum interface of the sample, for example, by reorientation, selective enrichment, or preferential accumulation of one or more components.

The C 1s spectrum of the 2H-TPP monolayer in Figure 5II displays one dominating peak at 284.9 eV (violet), which corresponds to the 44 aromatic C atoms in the porphyrin molecule, along with two shake-up satellites at 288.6 and 291.6 eV which are common for molecules with extended conjugated π systems. In the N 1s region, we find two
peaks (violet), one at 400.2 eV for the two pyrrolic (aminic, N–H) N atoms and one at 398.2 eV for the two iminic N atoms of the free-base porphyrin molecule. The ratio of $N_{\text{iminic}}/N_{\text{pyrrolic}}$ of 0.9 at 80° emission is somewhat smaller than the nominal ratio of 1.0. This difference is attributed to the so-called saddle-shape conformation of 2H-TPP on the Ag(111) and Au(111) surfaces. In this twisted conformation, the pyrrolic N–H moieties point toward the vacuum side and the iminic N atoms toward the metal surface. At 80° emission angle, this conformation could lead to an enhanced signal for the former and an attenuated signal for the latter because of inelastic scattering of the photoelectrons.

The deposition of 1.3 ML of [C8C1Im][PF6] on top of the porphyrin monolayer on Ag(111), Figure SIII, results in two new contributions in the C 1s region at 287.5 (gray) and 285.8 eV (yellow) because of the five C$_{\text{hetero}}$ atoms (i.e., carbon bound to nitrogen in the ring) and the seven C$_{\text{alkyl}}$ atoms (i.e., carbon bound to carbon and hydrogen in the chain) of the imidazolium cation. The additional N 1s peak at 402.6 eV (gray) corresponds to the two N atoms of the cation, and the F 1s peak at 687.3 eV (blue) corresponds to the six F atoms of the [PF6]$^{-}$ anion. The intensities of the porphyrin C 1s and N 1s signals strongly decrease upon IL deposition; the BEs of the IL-related peaks correspond very well to those of neat IL without any signs of decomposition. The residuals in the N 1s and C 1s regions (violet) are restored. This can be explained by complete desorption of [C8C1Im][PF6] from the surface, uncovering the intact porphyrin monolayer below the IL layer without any signs of decomposition.

For the Au(111) surface, we obtain very similar results, as is evident from Figure 6. In contrast to Ag(111), we note a slight shift of the porphyrin-related signals to higher BE and residual peaks, which seem to be related to the IL cation. The shift of the 2H-TPP-related N 1s and C 1s signals to higher BE after desorption could be a sign of dehydrogenation at the periphery of the 2H-TPP molecules. The residuals in the N 1s and C 1s regions could be interpreted as a result of decomposition of the IL in such a way that the [PF6]$^{-}$ anions are fully gone from the surface and fragments of the cation—perhaps as a result of carbene formation—remain. Similar residuals in the N 1s and C 1s spectra are also observed in slightly larger amounts upon desorption of this IL from bare Au(111), that is, in the absence of 2H-TPP.

In the next step, we studied the thermal stability of the composite films of IL on the porphyrin-covered metals by heating to 500 K. The corresponding results for the Ag(111) surface are shown in Figure SIV. After heating, the XPS signals related to [C8C1Im][PF6] (yellow, gray, and blue) disappear entirely, and the initial intensities of the porphyrin peaks in the C 1s and N 1s regions (violet) are restored. This can be explained by complete desorption of [C8C1Im][PF6] from the surface, uncovering the intact porphyrin monolayer below the IL layer without any signs of decomposition.

For the IL film on the 2H-TPP-covered Au(111), we also observe the complete removal of the anion-related F 1s signal after heating to 500 K on Au(111), as is evident from Figure 6IV. However, in contrast to Ag(111), we note a slight shift of the porphyrin-related signals to higher BE and residual peaks, which seem to be related to the IL cation. The shift of the 2H-TPP-related N 1s and C 1s signals to higher BE after desorption could be a sign of dehydrogenation at the periphery of the 2H-TPP molecules. The residuals in the N 1s and C 1s regions could be interpreted as a result of decomposition of the IL in such a way that the [PF6]$^{-}$ anions are fully gone from the surface and fragments of the cation—perhaps as a result of carbene formation—remain. Similar residuals in the N 1s and C 1s spectra are also observed in slightly larger amounts upon desorption of this IL from bare Au(111), that is, in the absence of 2H-TPP. These observations indicate that the decomposition occurs independently of the porphyrin interlayer. We carefully checked for potential influence of X-ray beam damage; but neither lowering the X-ray exposure from typically over 3 h for the whole heating series to less than 10 min before recording the final spectra after heating to 500 K nor varying the amount of IL deposited leads to notable changes in the amount of IL.
residuals formed upon desorption of the IL from bare and 2H-TPP-covered Au(111).

Interestingly, complete desorption of \([\text{C}_8\text{C}_1\text{Im}]\text{[PF}_6\text{]}\) with no signs of thermal decomposition has been observed for bare and 2H-TPP-covered Ag(111). Note that this is not generally the case on Ag(111), as thermal decomposition has been reported for an imidazolium-based IL with a partially fluorinated alkyl chain.\(^{35}\)

In the following, we take a closer look at the desorption processes on the bare and the 2H-TPP-covered Ag(111) and Au(111) surfaces. Figure 7 shows the thermal evolution of the IL F\(_{\text{PF}_6}\) signals (blue and orange) and the substrate signals (gray) from in situ temperature-programmed XPS at 0\(^\circ\) emission upon heating with a constant heating rate of 2 K/min.

On the bare metal surfaces (Figure 7a), the anion-related F\(_{\text{PF}_6}\) intensity stays nearly unchanged until about 385 K before it decreases to zero in two steps. The intensity of the respective Ag 3d and Au 4f signals increases accordingly. The first step with an inflection point at 405 K is attributed to the desorption of the IL multilayers, with a single WL of \([\text{C}_8\text{C}_1\text{Im}]\text{[PF}_6\text{]}\) remaining on the surface.\(^{34,35}\) From a Leading-Edge-like analysis\(^{307,147}\) of the data, we obtain an activation energy \(E_A\) of 167 kJ/mol (±18 kJ/mol) for multilayer desorption of \([\text{C}_8\text{C}_1\text{Im}]\text{[PF}_6\text{]}\), which is roughly in agreement with the value of 143 kJ/mol (±4 kJ/mol) published for \([\text{C}_8\text{C}_1\text{Im}]\text{[PF}_6\text{]}\) desorption from macroscopic IL samples.\(^{102}\) The second stepwise decrease in the intensity of the F\(_{\text{PF}_6}\) signal is in each case attributed to desorption of the remaining IL WL. Comparing the two graphs for the bare Ag(111) and Au(111) surfaces in Figure 7a, we observe desorption of the IL WL at a similar desorption temperature of about 445 K on both supports.\(^{34,35}\)

The similar desorption temperature of the IL WL from bare Ag(111) and bare Au(111) indicates a similar adsorption energy of \([\text{C}_8\text{C}_1\text{Im}]\text{[PF}_6\text{]}\) on both substrates. This behavior is surprising at first sight as Ag surfaces are generally considered more reactive than Au, an expectation that is based on the classic d-band center model, which was established around small molecules on metal surfaces.\(^{8}\) On the other hand, in light of the ionic nature of \([\text{C}_8\text{C}_1\text{Im}]\text{[PF}_6\text{]}\) and the larger polarizability of Au compared to Ag,\(^{8}\) one could expect a larger image dipole, yielding a larger adsorption energy on Au(111). Interestingly, very similar adsorption energies were also reported for structurally simpler aromatic molecules such as benzene on Ag(111) and Au(111).\(^{8,151,152}\) There, it was argued that the sensitivity of many-body contributions to the planar atomic density of face-centered cubic metals combined with the balance between Pauli repulsion and van der Waals forces between molecules and surface atoms can lead to very similar adsorption energies.\(^{8}\) Concerning the ILs studied here, we again note that on Au(111), the desorption of the IL WL from Au(111) goes along with a certain degree of decomposition (see above), which could also have an influence on the desorption behavior.

Next, we discuss the IL desorption on the 2H-TPP-covered surfaces in Figure 7b. The multilayer desorption of \([\text{C}_8\text{C}_1\text{Im}]\text{[PF}_6\text{]}\) is found to be identical to that on the bare surfaces. Interestingly, we do not observe the separate desorption of the WL at higher temperatures like on the bare surfaces. Instead, the entire IL film desorbs until 425 K, that is, at the same temperature as the multilayer. This desorption temperature of 405 K is about 40 K lower than the IL WL desorption temperature of 445 K on bare Ag(111) and Au(111) in Figure 7.

Figure 8. Spectra (80\(^\circ\)) of F 1s, C 1s, and N 1s core levels for (I) clean Ag(111), (II) after deposition of 1 ML of \([\text{C}_8\text{C}_1\text{Im}]\text{[PF}_6\text{]}\) at 84 K, (III) after direct deposition of a monolayer of 2H-TPP on top at 84 K, and (IV) after heating to RT. Color coding as in Figures 5 and 6.
7a. From this observation, we conclude that the interaction of \([C_8C_1Im][PF_6]\) with the 2H-TPP-covered surface is different from that with the bare metal surfaces. The 2H-TPP layer acts as a spacer between \([C_8C_1Im][PF_6]\) and the metals. It effectively inhibits the specific interaction of the IL WL with the metal, which leads to a pseudo-multilayer behavior of the IL WL on 2H-TPP. At this point, we need to mention that on the 2H-TPP-covered Ag(111) surface, the IL appears sensitive to the X-ray exposure accumulated prior to desorption. After exposing the system for more than 90 min, we observe that a fraction of the F 1s signal can remain up to 480 K (not shown), which we attribute to beam damage. Thus, the experiments had to be performed with minimum exposure to X-rays.

After the complete desorption of the IL at 500 K, the intact porphyrin layer is retained on Ag(111) (compare Figure 5IV to 5II), as already mentioned above. On Au(111), the residual cation-related XPS signals at 500 K on Au(111) (compare Figure 6IV to 6II) hint at a lower stability of the cation-related XPS signals at 500 K on Au(111) (compare Figure 5IV to 5II) as a result of decomposition. As already mentioned above, also the desorption of the IL from bare Au(111) shows similar residuals in C 1s and N 1s, indicating that there is no direct influence of the 2H-TPP layer on the decomposition of the IL.

### 3.3. Deposition at LT and Exchange of \([C_8C_1Im][PF_6]\) by 2H-TPP at the IL/Metal Interface.

To further extend our understanding of the interaction of \([C_8C_1Im][PF_6]\) and 2H-TPP at the interfaces of Ag(111) and Au(111), the order of the deposition process was reversed. We first deposited 1 ML of \([C_8C_1Im][PF_6]\) at LT (80–84 K), followed by a single layer of 2H-TPP directly on top of the IL layer, again at LT. This composite film was subsequently heated to RT. XP spectra were measured after each preparation step.

Figure 8 shows the F 1s, C 1s, and N 1s spectra at 80° for this deposition experiment on Ag(111) at 84 K. Figure 9 provides a scheme of the film structure at different stages of this experiment. The F 1s spectrum in Figure 8II after deposition of the \([C_8C_1Im][PF_6]\) film (1 ML) shows the expected FPF6 peak of the \([PF_6]\)

The spectra after deposition of 2H-TPP onto the IL film at 84 K in Figure 8III show a pronounced attenuation of all IL-related XPS signals. We also find two additional peaks in the N 1s and one in the C 1s spectrum related to the two inequivalent nitrogen species and the carbon in 2H-TPP. The spectra clearly indicate that the 2H-TPP molecules remain at the vacuum interface at this LT and cover the IL film underneath; see Figure 9III.

Upon heating to RT, we observe several changes in the XP spectra in Figure 8IV. All IL-related contributions gain intensity—the C alkyl peak shows a particularly strong increase—whereas at the same time, the 2H-TPP signals decrease substantially. We attribute these changes to the diffusion of 2H-TPP molecules to the Ag(111) surface and replacement of the IL at the interface to the metal. As a result, \([C_8C_1Im][PF_6]\) forms the new IL/vacuum interface of the film; see Figure 9IV. Notably, at RT, the FPF6, N cation, and C hetero signals at 80° are lower than they were in the spectra of the film of pure \([C_8C_1Im][PF_6]\) on Ag(111) at 84 K. This is due to the strong enrichment of the alkyl chains at the vacuum interface at RT, which is not observed after the deposition of the IL at 84 K, because of lack of mobility. The ratio of C hetero/C alkyl of 0.41 at RT in Figure 8IV is similar to the value of equally thick films of pure \([C_8C_1Im][PF_6]\) directly on Ag(111) (see also Figure S1 in the Supporting Information).

To further elucidate this exchange process, we monitored the thermal evolution of the F 1s and C 1s peak intensities by in situ temperature-programmed XPS at 80° emission; see Figure 10. After the deposition of one layer of 2H-TPP on 1 ML of \([C_8C_1Im][PF_6]\) at 84 K, the layered film was heated from 84 K to RT with a heating rate of 2 K/min. All intensities remain constant up to about 215 K. Thereafter, the FPF6 signal decreases substantially. We attribute these changes to the diffusion of 2H-TPP molecules to the Ag(111) surface and replacement of the IL at the interface to the metal. As a result, \([C_8C_1Im][PF_6]\) forms the new IL/vacuum interface of the film; see Figure 9IV. Notably, at RT, the FPF6, N cation, and C hetero signals at 80° are lower than they were in the spectra of the film of pure \([C_8C_1Im][PF_6]\) on Ag(111) at 84 K. This is due to the strong enrichment of the alkyl chains at the vacuum interface at RT, which is not observed after the deposition of the IL at 84 K, because of lack of mobility. The ratio of C hetero/C alkyl of 0.41 at RT in Figure 8IV is similar to the value of equally thick films of pure \([C_8C_1Im][PF_6]\) directly on Ag(111) (see also Figure S1 in the Supporting Information).

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increases by almost 70% until 255 K. Simultaneously, the C\textsubscript{Alkyl} signal of the \([\text{C}_8\text{C}_1\text{Im}]^+\) cation also increases by more than 100%, whereas the porphyrin-related C 1s contribution decreases to 40%. From this behavior, we conclude that the exchange of the IL molecules by the 2H-TPP molecules at the Ag(111) interface occurs at about 240 K.

The main driving force for the exchange at the metal interface very likely is the considerably larger adsorption energy of 2H-TPP on the metal surface compared to \([\text{C}_8\text{C}_1\text{Im}]^+\); the IL WL desorbs at around 445 K, whereas 2H-TPP does not desorb until decomposition occurs at temperatures above 525 K.\textsuperscript{9,122,123} For comparable exchange processes between different ILs, involving \([\text{C}_8\text{C}_1\text{Im}]^+[\text{PF}_6]^-\)/Ag(111),\textsuperscript{34,35} the surface tension at the vacuum interface was determined rather by the properties of the porphyrin layer at the IL/metal interface, and not by the IL layer below, which should have enough mobility already at a lower temperature. This observation indicates that the exchange process is laterally by strong phenyl−phenyl bonds.\textsuperscript{96,97,122,123,132} Indeed, Chen et al. showed that confinement of a closely related IL, \([\text{C}_8\text{C}_1\text{Im}]^+[\text{PF}_6]^-\), in multiwalled carbon nanotubes led to a considerable increase in the melting point of the IL, where shorter than usual C−H−F contacts can be formed.\textsuperscript{156}

Another possibility for the shift of the transition to higher T could be the higher activation energy. Because of the larger size of the porphyrin molecule, two ion pairs need to be replaced at the IL/metal interface for one porphyrin molecule instead of only one cation or anion (as in the case of the previously mentioned IL/IL films on Ag(111)).\textsuperscript{34,35}

For the corresponding experiment on Au(111), we again monitor the F 1s, N 1s, and C 1s signals at 80\textdegree; see Figure 11. After deposition of 1 ML of \([\text{C}_8\text{C}_1\text{Im}]^+[\text{PF}_6]^-\) on Au(111) at 80 K, the ratio of C\textsubscript{hetero}/C\textsubscript{alkyl} of 0.63 in Figure 11III is again quite close to the nominal ratio of 0.71 (=5:7). The spectra after the deposition of a single layer of 2H-TPP on top of the IL film in Figure 11III show the porphyrin-related N 1s and C 1s contributions in the expected quantities and a strong attenuation of the IL signals, which again indicate that the porphyrin molecules cover the IL film. Upon heating to RT, the IL-related peak intensities in Figure 11IV increase again, whereas the porphyrin signals lose intensity. With a ratio of C\textsubscript{hetero}/C\textsubscript{alkyl} of 0.40 at RT, the alkyl chain enrichment is similar to that on 2H-TPP-covered Ag(111) and also to that of macroscopic films of \([\text{C}_8\text{C}_1\text{Im}]^+[\text{PF}_6]^-\) (see also Figure S1 in the Supporting Information). We therefore conclude that on Au(111) also, the IL at the metal surface is replaced by porphyrin upon heating to RT.

4. SUMMARY AND CONCLUSIONS

Studying the interaction of the porphyrin 2H-TPP and the IL \([\text{C}_8\text{C}_1\text{Im}]^+[\text{PF}_6]^-\) on Ag(111) and Au(111) by ARXPS, we demonstrate for the first time that well-defined bilayered porphyrin/IL film systems stable up to above 100\textdegree; can be produced on both metal surfaces by means of PVD under UHV conditions. Starting with a monolayer of 2H-TPP, we observe the growth of a closed 2D \([\text{C}_8\text{C}_1\text{Im}]^+[\text{PF}_6]^-\) WL on top of the 2H-TPP-covered metal surfaces. Further IL deposition leads to the formation of 3D islands on top of this WL; this Stranski−Krstanov-like IL growth behavior is less pronounced when \([\text{C}_8\text{C}_1\text{Im}]^+[\text{PF}_6]^-\) is deposited directly on bare Ag(111) and Au(111). Heating the bilayered IL/2H-TPP films to about 385 K does not lead to film intermixing; above this temperature, the IL layer starts to desorb. Similar to \([\text{C}_8\text{C}_1\text{Im}]^+[\text{PF}_6]^-\) multilayers, the IL on the 2H-TPP-covered metals desorbs entirely below 425 K. This contrasts the situation on the bare Ag(111) and Au(111) surfaces, where in the absence of 2H-TPP, a clear separation between the
desorption of the multilayers and the IL WL in direct contact to the metal was observed. We assume that the porphyrin layer decouples the IL from the metal surfaces, effectively inhibiting the stronger specific adsorption of the ions. After IL desorption, the 2H-TPP layer remains on the surface. In contrast to Ag(111), we observe signs of thermal decomposition of the IL on Au(111) and 2H-TPP/Au(111) in the course of heating, leaving cation-related residuals behind.

After deposition of 2H-TPP on top of a frozen film of \([C_8C_1Im][PF_6]\) at around 80 K, the 2H-TPP layer covers the IL film below. Upon heating, the porphyrin molecules replace the IL at the IL/metal interface at around 240 K. This exchange process is most likely driven by the higher adsorption energy of 2H-TPP on the Ag(111) and Au(111) surfaces as compared to the IL. With reference to earlier studies \(^{34,35}\), we assume that this temperature of 240 K is determined by the onset of mobility of the porphyrin layer.

Our studies on the replacement of IL layers at the IL/metal interface by postdeposition of porphyrins or comparable organic species are highly relevant for the understanding of processes in the liquid phase. In a way, our UHV-based experiment mimics preferential (selective) adsorption of porphyrins on the corresponding substrates from a diluted porphyrin solution. As the deposition from the liquid phase can follow completely different mechanisms from the deposition from the gas phase, the resulting surface structures of the porphyrin layer could be quite different. Such replacement effects are closely related to stability issues of IL-related catalytic systems: on the one hand, poisoning of a SCILL catalyst through adsorption of molecular reagents similar to 2H-TPP could irreversibly block the support surface and would lower the effectiveness of the catalyst over time, similar to poisoning of Pt catalysts by sulfur or other nonreactive species.\(^ {159-162}\) On the other hand, SILP systems using catalytic centers based on metalloporphyrin derivatives\(^ {18} \) could face major challenges if the complexes preferentially adsorb to the support surface and thus are depleted from the liquid phase. The system would lose the characteristic homogeneous nature of the catalyst and possibly diminish its reactivity/selectivity. From an even more general point of view, the observed exchange is also relevant for the stability of organic–organic heterostructures on solid supports. When a device (like a porphyrin-based field-effect transistor) is prepared at one temperature but used at higher temperatures, the increased mobility of the molecules could change the intended structure/organization of the layered film stack.

**ASSOCIATED CONTENT**

▲ Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpcc.9b08531. Molecular orientation during the growth of \([C_8C_1Im]-[PF_6]\) on Ag(111) and Au(111), deposition of 2H-TPP on an IL-covered 2H-TPP monolayer, and residuals on Au(111) after IL desorption compared to Ag(111) (PDF)

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