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Polymerization of Heteroleptic Amphiphilic Osmium(II) Complexes at the Air/Water Interface: Attempts Toward Nanoarchitectonics in Form of Molecular Textiles

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ABSTRACT

The controlled construction of interwoven molecular architectures via metal coordination represents a promising strategy for the development of ordered, interwoven, two-dimensional (2D) materials. Here, we report a bottom-up approach to probe the relationship between molecular symmetry and interfacial 2D polymerization behavior. Two amphiphilic heteroleptic osmium(II) terpyridine complexes were designed that incorporate aldehyde and amine functionalities, asymmetric complex (**1**), capable of forming two imine bonds, and a symmetric analog with four reactive sites (**2**). Langmuir–Blodgett isotherms, Brewster angle microscopy confirmed monolayer formation. In noncontact atomic force microscopy images **1** produced discrete oligomeric aggregates, while **2** yielded extended, chain-like polymeric structures with high surface coverage. X-ray photoelectronic spectroscopy measurements supported the presence of polymers as a product of imine condensation. Density functional theory calculations of **1** and its dimer and tetramer were performed to assess the stability of motifs relevant to the supramolecular structures observed. Comparison of the oligomers indicates a slight thermodynamic preference for chain-like growth over crosslinking. Although these calculations are limited, the intrinsic bias toward linear linkages is consistent with atomic force microscopy data. Together, these results suggest polymer formation through imine condensation on the water–air interface, yielding kinetically favored chain formation and expanded 2D connectivity.

1 | Introduction

Nanoarchitectonics describes the building of functional materials at nanoscale by implementing the structural information at the atomic level by molecular design [1, 2]. Here, the concept is applied to form molecular textiles. Since the conceptualization of interwoven materials at the molecular scale by Bush in 1992 [3], various strategies have been developed to construct such systems using metal coordination as templates [4–6]. For example, Li et al. and Han et al. utilized the coordination sphere of metal

centers to link strands, thereby generating interwoven structures composed of one-dimensional (1D) coordination polymers [7, 8]. In these approaches, the overall woven architecture is stabilized by metal–ligand interactions.

To create structures that entangle organic 1D polymers, molecular knots were assembled via metal coordination as an organizing template [9–12]. Another way to introduce woven units is through rigid ligands designed with opposing coordination sites. Upon complexation, such ligands can produce interwoven patches, as

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explored by Schäfer et al. and Suryadevara et al. [13, 14] Leigh et al. further extended these ideas by forming a 7₄-knot [15] featuring an interwoven grid. A structural motive that enabled them to produce a two-dimensional interwoven polymeric material via intermolecular interlinking of peripheral functionalized units [16]. Yaghi et al. advanced the concept of preorganizing metal complexes, which formed each “knot” in the polymer network, which can be linked via linear building units to yield two- or three-dimensional interwoven frameworks, depending on monomer planarity [17, 18]. A valuable method for the fabrication of films of vertically organized molecules is the Langmuir–Blodgett (LB) technique developed in the early 20th century. Initially designed to form and transfer monolayers of fatty acids from the air–water interface onto solid substrates [19, 20], this technique enables the fabrication of thin films with controllable packing density by compressing monomers at the interface between both phases. The LB method has been employed, for example, to construct 2D metal–organic frameworks by spreading organic linkers on the water surface, where they coordinate with metal ions in the aqueous subphase to yield monolayers of 2D coordination polymers [21–23]. Also, covalent organic 2D monolayers were synthesized with this technique by the formation of various bonds on the water surface [24–27].

A popular interlinking strategy for interfacial polymerization is based on reversible imine condensation, which is due to its dynamic nature [28–30] vastly employed in the self-assembly of molecular architectures like cages, shape-persistent macrocycles and polymer frameworks [31–34]. In spite of the large water concentration at the interface which might favor the separation into amine and aldehyde in the equilibrium with the imine linker, such condensations between two complementary monomers, bearing either aldehyde or amine functionalities, were already realized successfully at the water–air interface [35–38].

2 | Results and Discussion

2.1 | Strategy and Design

Figure 1 displays the discussed complexes (Figure 1a,e) and sketches the intended strategy toward molecular textiles. As sketched in Figure 1a–d, the long-term plan is to assemble the interwoven material via a bottom-up approach using a single monomer. This monomer contains both reactive functional groups, and their spatial arrangement is preorganized through metal coordination. A molecular monolayer shall be obtained by spreading the monomer at the air/water interface (Figure 1b), where hydrophobic and hydrophilic termini shall control the vertical orientation of the monomer. With the vertically aligned monomers and ideal tuning of their density in the LB trough, lateral polymerization is achieved by imine condensation. Particular appealing is the reversibility of the condensation, as it holds the potential of an intrinsic error-correction mechanism. The intention is to obtain a highly ordered, periodic, chess-board-type 2D monolayer of imine-interlinked complexes (Figure 1c). As consequence of the vertical orientation at the air/water interface, all monomers expose the aldehyde-functionalized terpyridine ligand to the air and thus, in order to achieve the proximity of aldehyde and amine required for imine formation, in a pair of

neighboring complexes, one must revolve by 90° with respect to the other. In case of a chess-board-type 2D polymer, the linear strands formed by the imine-interlinked ligands are arranged in a periodic up-down pattern, resembling a macroscopic textile. Thus, subsequent decomplexation is supposed to provide a molecular textile formed by mechanically interwoven linear strands (Figure 1d).

The design of the target structures **1** and **2** is deduced from the above-described strategy (Figure 1e,a). Heteroleptic M²⁺ terpyridine (2,2':6',2''-terpyridine) complexes are ideally suited for the approach. Their charge provides water solubility, while the hydrophobicity of each ligand can be tuned by the small oxy-substituent in the 4'-position. The 1,3-dimethoxy-propan-2-oxy-substituent is expected to interact with the aqueous phase, while the isopropoxy-substituent increases the ligands hydrophobicity. With the vertical orientation fixed, the lower water-soluble terpyridine ligand was decorated with the amine groups in 5 and 5'' positions. The rationale was that the acidic media catalyzing the imine formation might temporarily protonate the amine group, further increasing the ligand's hydrophilicity. The second upper terpyridine ligand was functionalized with aldehydes in 5 and 5'' positions. In the heteroleptic M²⁺ coordination complex, the reactive groups are located pairwise at the termini of both perpendicularly arranged ligands and thus remote enough to make intramolecular imine formation impossible. As coordination metal ion (M²⁺), osmium(II) was chosen because of the well-defined octahedral geometry of its terpyridine complexes and their high stability. While the strategy toward molecular textiles comprises the removal of the coordinating ion after 2D polymerization, robust complexes were favored for the here reported preliminary studies of the surface polymerization behavior of the monomers. In contrast to our preliminary studies with iron(II) terpyridine complexes, the stability of the here reported osmium complexes enables the investigation of the polymerization process without concern of metal–ligand dissociation, neither during the polymerization nor during storage.

The success of the imine formation between monomers at the air/water interface depends on their proximity, which can be adjusted by the compression of the molecular film in the LB trough (Figure 1b,f). An alternative strategy to reduce both the likeliness of imine formation and the complexity of the system is to reduce the amount of exposed functional groups. Complex **1** (Figure 1e) exposing only one amine and aldehyde, respectively, was considered as simpler model system to study the monomer coupling in the LB experiment. The reduced C₁ symmetry of **1** compared to the C₂ symmetry of **2** is reflected in the expected polymers. As sketched in Figure 1g, the bifunctional monomer **1** not only results in linear polymers but also the formation of macrocyclic oligomers, enabling all terminal functional groups to participate in imine coupling reactions. Interestingly, the vertical preorganization at the air/water interface should result exclusively in macrocycles consisting of an even number of monomers like, for example, the displayed dimers and tetramers. Decomplexation of these poly- and oligomers of **1** would not allow to make conclusions about the dimensions of the macromolecules, as all compounds would result in the same imine interlinked combination of both terpyridine ligands. The macromolecules were thus transferred on a solid substrate (Figure 1h) to be analyzed by scanning probe methods.

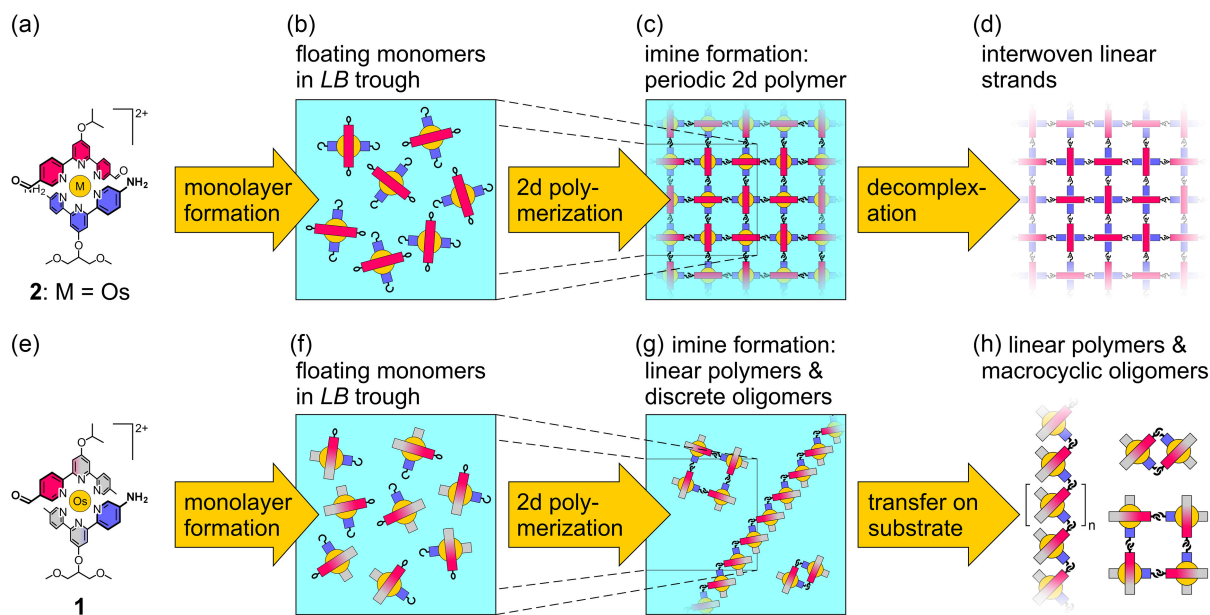


FIGURE 1 | Concept of the assembly of a molecular textile from complex **2** preorganized at the air/water interface and of macrocyclic oligomers from complex **1**. Structure of the tetrafunctional complex **2** (a), its deposition at the air/water interface (b), and the chess-board type 2d polymer expected from its imine condensation (c). The molecular textile (d) obtained by decomplexation of the chess-board type 2d polymer. Structure of the bifunctional complex **1** (e), its deposition at the air/water interface (f), and the linear polymers or macrocyclic oligomers formed upon imine condensation (g), which can be peeled from the water surface for analysis purposes (h).

With the two complexes exposing different numbers of functional groups, a stepwise study is envisaged to investigate interdependences between molecular symmetry, reactive functionalities, and interfacial polymerization behaviors. In the following section, the syntheses of the corresponding ligands and complexes are described, followed by the study of their polymerization behaviors at the air/water interface and the subsequent investigation of the observed macromolecules.

2.2 | Synthesis

For the amphiphilic asymmetric heteroleptic complex **1**, two asymmetric terpyridine ligands were synthesized (Figure 2a). The ligands were constructed stepwise by *Stille* coupling reactions, starting with the functionalization of compound **4** with either a hydrophilic group (for ligand precursor **3**) or a hydrophobic group (for ligand precursor **5**). These surface-directing substituents were introduced through *Mitsunobu* reactions in good yields of 84% and 74%, respectively. An amine functionality was introduced in a Boc-protected form at the 5-position of pyridine derivative **6**. Compound **6** was subsequently converted to **7** via lithium-halogen exchange, followed by stannylation. Its aldehyde analog, **10**, was synthesized in two steps by protecting the aldehyde group of **8** with a 1,3-dioxolane acetal with an adapted reported procedure [39], affording **9** in excellent yield (93%). Subsequent bromine–lithium exchange and stannylation furnished another *Stille* coupling building block, **10**.

The hydrophobic asymmetric ligand **12** was assembled through a one-fold *Stille* coupling between **5** and **10** (1:1 ratio) to yield **11** in moderate yield of 40%. A final coupling with a 5-methyl-2-(tri-*n*-butylstannyl)pyridine unit afforded the target ligand **12** in good yield of 80%.

For the hydrophilic ligand **14**, a one-fold *Stille* coupling between **3** and 5-methyl-2-(tri-*n*-butylstannyl)pyridine provided **13** in fair yield of 60%. Introduction of the amine functionality was achieved by coupling **13** with **7**, affording the final ligand **14**. To form heteroleptic complex **15**, $(\text{NH}_4)_2\text{OsCl}_6$ and **12** were complexed in a 1:1 ratio at 120 °C to first form an intermediate with one terpyridine ligand. In the next step, **14** was added at 180 °C to form the final heteroleptic complex **15**, which was then isolated by reversed-phase high-performance liquid chromatography (HPLC) in 22%. The boc-amine of **14** was deprotected thermally under the applied temperature. Complex **15** forms two enantiomers, whose separation is currently under investigation.

The hydrophilic terpyridine ligand **18** was synthesized starting from terpyridinol **16** (Figure 3a). The hydroxy group of **16** was then transformed to an ether with 1,3-dimethoxy-2-propanol via a Mitsunobu reaction, providing **17** in a fair yield of 73%. To install the boc-protected amine groups, a Buchwald–Hartwig type cross-coupling with *tert*-butyl carbamate was performed, and **18** was obtained in reasonable 60%. Hydrophobic ligand **19** was synthesized via a *Stille*-cross coupling of two equivalents of **10** and one equivalent of **5** in very good yield.

First, the ligand **19** was complexed with the osmium salt, and the mono-terpyridine complex was isolated before ligand **18** was added at higher temperature of 180 °C to form the heteroleptic complex **20**, which was isolated by precipitation with aq. sat. KPF_6 followed by purification over reversed-phase HPLC.

Prior to the surface investigations, the complexes **1** and **2** were formed by deprotecting **15** and **20** by stirring the monomers with CH_3CN and aq. HCl , followed by neutralization with aq. NaOH and precipitation with aq. sat. KPF_6 .

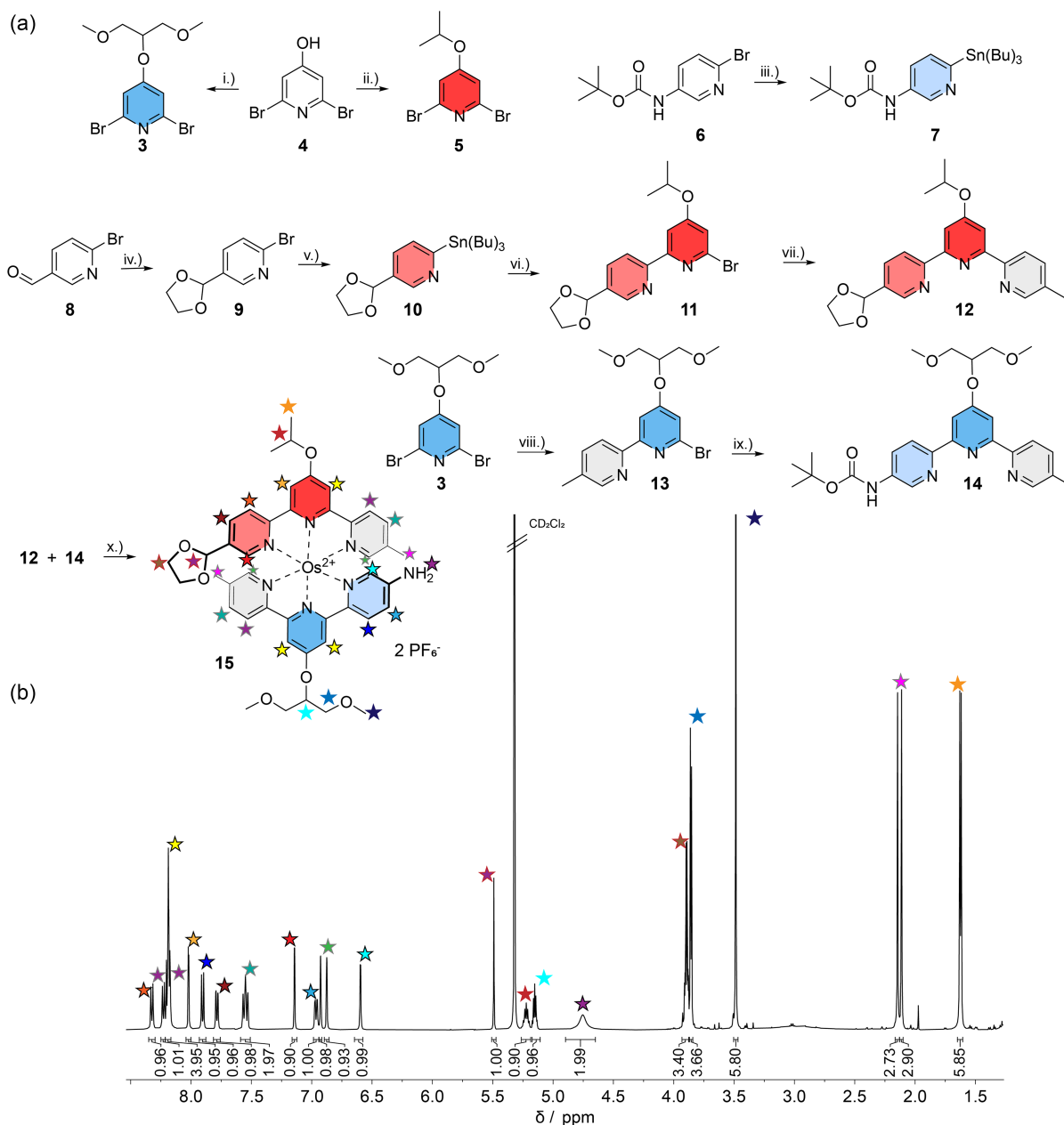


FIGURE 2 | (a) Synthesis of complex 15. Reagents and conditions: i) DIAD, PPh₃, 1,3-dimethoxypropan-2-ol, THF, 0 °C – rt, 5 h, 84%; ii) DIAD, PPh₃, 1,3-dimethoxypropan-2-ol, THF, 0 °C – rt, 18 h, 73%; iii) *n*-BuLi, Sn(Bu)₃Cl, THF, –78 °C – rt, 4 h, 40%; iv) Ethyleneglycol, *p*-TsOH, ACN, 120 mbar, 40 °C, 93%; v) *n*-BuLi, Sn(Bu)₃Cl, THF, –78 °C – rt, 8 h, 40%; vi) 5, Pd(PPh₃)₄, Toluene, 90 °C, 18 h, 40%; vii) 5-Methyl-2-(tri-*n*-butylstannyl)pyridine, Pd(PPh₃)₄, Toluene, 120 °C, 18 h, 79%; viii) 5-Methyl-2-(tri-*n*-butylstannyl)pyridine, Pd(PPh₃)₄, Toluene, 90 °C, 18 h, 60%; ix) 7, Pd(PPh₃)₄, Toluene, 120 °C, 18 h, 78%; x) (NH₄)₂OsCl₆, ethyleneglycol, 120 °C, 2 h, then ethyleneglycol, 180 °C, mw, 1 h, 22%; (b) ¹H-NMR spectrum of 15 in CD₂Cl₂ 500 MHz with its assigned protons.

Detailed synthetic protocols and analytical data of the new complexes (Figures 2b and 3b), their ligands, and their precursors are provided as Supporting Information.

2.3 | Solid-State Structure of 1

To corroborate its structural identity and to evaluate the spatial arrangement of the functional groups, the solid-state structure of asymmetric complex 1 was investigated by X-ray diffraction (Figure 4). Single crystals suitable for X-ray diffraction analysis were obtained as small, purple-colored needles by slow diffusion

of toluene into an acetonitrile solution of 1, followed by slow evaporation. Complex 1 crystallizes in a monoclinic *C2/c* space group as a racemic mixture of enantiomers with 2 PF₆[–] counterions. In the solid state, the height of the complex was determined to be 15.5 Å. As intended by molecular design, the planes of the two terpyridine ligands, each comprising either the amine or the aldehyde, are with an angle of 91.7° almost orthogonally oriented to each other. The lateral dimensions of complex 1 are 12.1 Å × 10.8 Å, as shown in Figure 4b.

In the crystal packing, the complexes are arranged in a head-to-head and tail-to-tail fashion, thereby segregating the hydrophilic

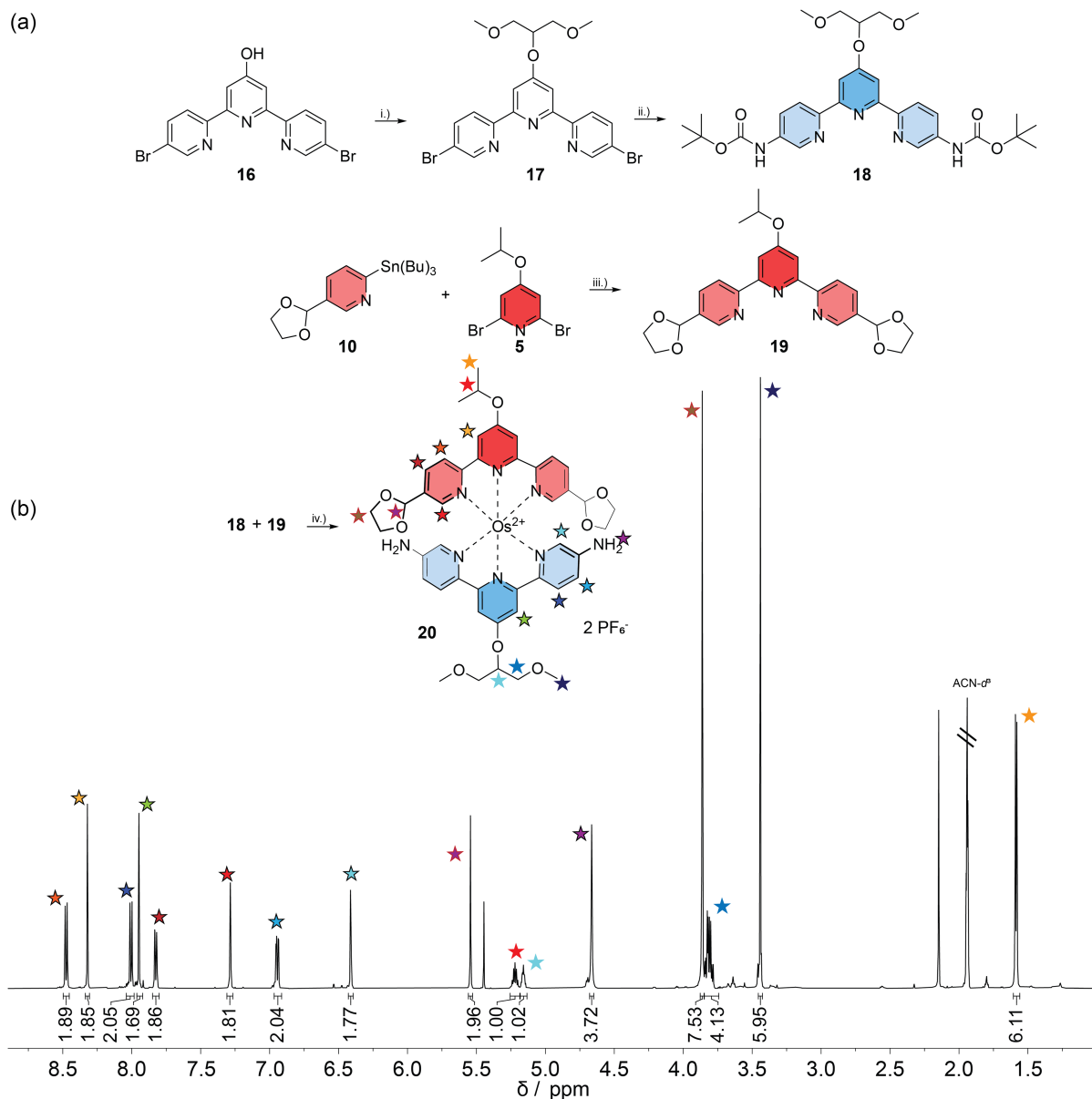


FIGURE 3 | (a) Synthesis of complex **20**. Reagents and conditions: i.) DIAD, PPh_3 , 2-Propanol, THF, 0°C – rt, 18 h, 73%; ii) *tert*-Butylcarbamate, $\text{Pd}_2(\text{dba})_3$, Xantphos, CsCO_3 , dioxane, 85°C , 12 h, 60%; iii.) $\text{Pd}(\text{PPh}_3)_4$, Toluene, 120°C , 18 h, 90%; iv.) $\text{OsCl}_6(\text{NH}_4)_2$, ethyleneglycol 120°C , 5 h, then **19**, ethyleneglycol, 180°C , 1 h, 20%; (b) ^1H -NMR spectrum of **20** in ACN-d_6 at 500 MHz with its assigned protons.

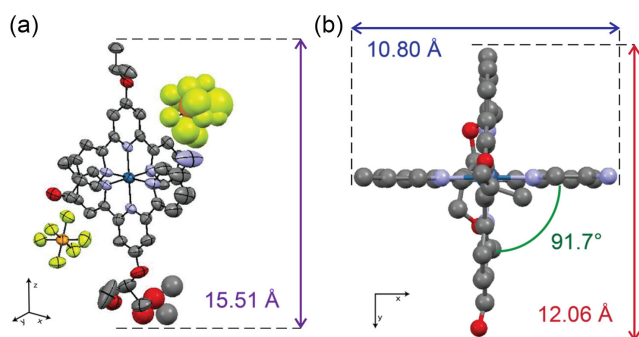


FIGURE 4 | Solid-state structure of **1**. Hydrogen atoms are omitted for clarity. (a) ORTEP plot with counterions at 50% probability, side view and (b) birds eye view with omitted counterions. The dimensions of the complex are indicated by colored arrows.

and hydrophobic regions. This packing motif is promising with respect to the intended interfacial alignment approach, in which the complexes are expected to orient similarly at the air/water interface, with the hydrophobic substituents directed toward the air and the hydrophilic groups toward the aqueous phase.

2.4 | Polymerized Monolayers

With the desired geometry of our complexes confirmed, their self-assembly on the air/water interface was investigated. C_2 symmetric complex **2**, exposing two amines on one terpyridine ligand and two aldehydes on the other, is capable of forming imine bonds at all four termini and was thus expected to assemble into a 2D polymeric network (Figure 1c). The bifunctional asymmetric complex **1** on the other hand, exposes only one amine and

aldehyde on its ligands, and consequently either linear polymers or cyclic oligomeric structures were expected (Figure 1g). To examine their packing and behavior at the air/water surface, Langmuir–Blodgett compression isotherms were recorded, while the molecular layers were observed by Brewster angle microscopy (BAM). The monolayers obtained were then transferred via Langmuir–Blodgett deposition onto highly ordered pyrolytic graphite (HOPG) samples, and the deposited structures were further analyzed by atomic force microscopy (AFM).

As bifunctional complex **1** can only provide 1D motives like the above-mentioned linear chains or macrocycles, it served as model compound for the investigation of the surface behavior of these amphiphilic complexes. A solution of **1** dissolved in $\text{CH}_3\text{CN}:\text{CH}_2\text{Cl}_2:\text{CF}_3\text{CO}_2\text{H}$ (5:11:0.01) was cast on the water surface of the *LB* trough. The acidic conditions are expected to support imine formation between the monomers in the molecular layer. Compression isotherms of asymmetric complex **1** showed that it formed well-defined monolayers without significant variation in the pressure/area isotherms across different loadings (Figure 5). Surface pressure increased proportionally with the amount of material spread, and BAM images showed that the contrast increased at low pressures (0–1 mN m^{-1}), indicating early aggregation at low compression. The raise of the compression isotherms was reproducibly observed at ca. $7 \text{ \AA}^2$. As the area of the monomer as tile of the chess-board arrangement would be significantly larger (ca. $100 \text{ \AA}^2$), the value points at an intercalation of the monomers under compression. Most likely, the monomers fill out the intermonomer space before building up the resistance required to raise the surface pressure. The molecular layer formed at 2 mN m^{-1} was deposited on a HOPG sample via X-type deposition and pushed in with a speed of 3 mm/min . The sample was transferred into the UHV chamber of the AFM and analyzed using the noncontact mode (nc-AFM). A uniform coverage of the HOPG sample was observed.

Disorganized monolayers of complex **1** with dimensions of a few hundred nanometers were detected on the HOPG surface. Large islands with a height of 1.2 nm are observed in the whole sample, with parts of the HOPG surface remaining free from the molecular layer (see arrow in Figure 5b). The recorded height correlates reasonably well with the dimension of complex **1** determined

in the solid state (Figure 4a). More details of the monolayer's structure can be observed in the second pass frequency shift images [40–42], like the zoom of the molecular layer displayed in Figure 5c. More or less well-defined, discrete, cloud-shaped objects spread over $5\text{--}25 \text{ nm}^2$ could be observed. Considering the dimension of the monomer, it is tempting to hypothesize that these objects are covalent assemblies of 2–6 monomers. The monolayer clearly lacks a large-scale order and consists of a variety of structures, most likely made of covalently interlinked complexes. Furthermore, the limited resolution of the analytical method did neither allow us to resolve the individual building blocks nor to assign the numbers of monomers particular objects were made of.

Similar *LB* experiments with the fourfold functionalized complex **2** were performed using more acidic conditions to improve the compounds solubility. It is noteworthy that the deprotection of the acetal-protected form **20** to the liberated complex **2** reduced its solubility substantially, most likely due to an exchange of counter ions during the deprotection process. In a first attempt, the complex was cast to the water surface dissolved in $\text{CH}_2\text{Cl}_2:\text{CF}_3\text{CO}_2\text{H}$ (1:1). Interestingly, compression isotherms of **2** (Fig. S3a) were comparable in shape to complex **1** but displayed concentration-dependent shifts of the surface-pressure onsets. Most likely, these shifts were triggered by the variation of the subphase acidity, which reached pH 5 at the highest amount of cast stock solution (69 nmol). As an alternative explanation, imine formations in the stock solution were considered. However, the stock solution was monitored by mass spectrometry, and neither showed dimer formation nor precipitations expected for larger oligomers. Promisingly, compared to complex **1**, stronger BAM contrasts were recorded with increasing surface pressures. Already at low pressure, the BAM signal pointed at denser molecular packing, the desired behavior of the fourfold decorated model compound. While close packing is expected to be beneficial for the formation of the 2D polymer by lateral imine formation, we were also afraid that excessive compression might handicap the imine formation by pushing the functional groups into the empty voids in between the terpyridine ligands of the complex. Consequently, a medium packing density at 1 mN m^{-1} pressure was chosen for deposition of the molecular film on the HOPG sample. After transfer into the UHV chamber, nc-AFM analysis revealed domains with high density of polymers (Figure 6a,b)

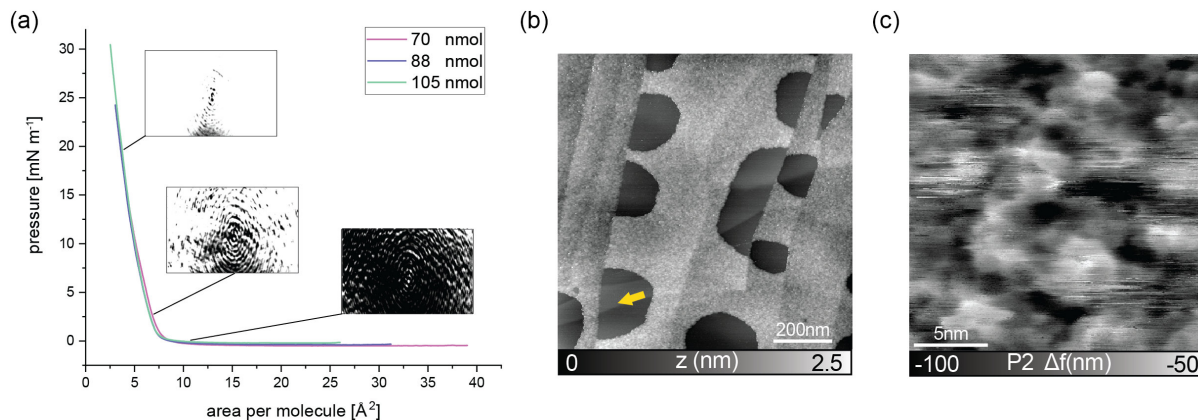


FIGURE 5 | Surface analysis of bifunctional complex **1**. (a) Compression Isotherms of **1**; (b) nc-AFM Topography of a HOPG surface coated at 2 mN m^{-1} in UHV conditions; $f_1 = 177 \text{ kHz}$, $A_1 = 6 \text{ nm}$, $\Delta f_1 = -30 \text{ Hz}$; (c) Second pass frequency shift nc-AFM image parameters: (b,c) $f_1 = 177 \text{ kHz}$, $A_1 = 6 \text{ nm}$, $\Delta f_1 = -30 \text{ Hz}$, (c) $\Delta z = -300 \text{ pm}$.

with a height of 2 nm (Figure S3c), consistent with molecular monolayers. The polymer structures observed on the surface are long, occasionally cross-linked chains. While the observed branching of the polymer chains results in a 2D network resembling the desired 2D polymer, the rather moderate number of branching points shows how remote the system still is from forming a compact 2D polymer with every monomer acting as tile being fourfold connected with its nearest neighbor. However, the sheer existence of these links is an exciting discovery, as they increase the overall surface coverage, bringing the entire system one step closer to the aimed for regular, extended 2D polymer monolayer.

To increase the number of crosslinks in the 2D network, a less acidic spreading solution in the *LB* process was considered. The hypothesis was that protonated amines don't react as nucleophiles with the neighboring aldehydes and that reduced acidity will increase the number of amines engaged in cross-linking. Thus, complex **1** was cast with $\text{CH}_2\text{Cl}_2:\text{CH}_3\text{CN}:\text{CF}_3\text{CO}_2\text{H}$ (4:3:1). The resulting isotherms (Figure S4 a) showed improved reproducibility and a smaller shift in the onset of surface pressure increase. To further compress the monomers on the water surface, the surface pressure was slightly increased to 1.2 mN m^{-1} for the deposition of the molecular layer on the HOPG sample. After transferring into the UHV chamber of the AFM, nc-AFM images (Figure 6c) indeed revealed substantially denser surface coverage. Whether the higher coverage emerges exclusively from increased cross-linking or is in part resulting from more condensed packed linear polymer chains can't be distinguished by the analytical technique. However, higher compression might encourage higher intramolecular reactions, resulting in an increased number of cross-links. The measured height of 1.1 nm (Figure S4c) again matched a monolayer of **2**, supporting higher surface coverage by polymerization under milder conditions.

To further analyze the molecular depositions observed on the nc-AFM images, their chemical nature was investigated by X-ray photoelectron spectroscopy (XPS). XPS spectra of the Si wafers coated with the monolayers transferred from the air/water interface were recorded and displayed signals displaying the presence of C, N, O, and Os, as expected for films emerging from the monomeric osmium complex **2** (Figure S5). To gain further details about the level of imine formation interlinking the monomers, the N 1s region of the deposited films was compared with those of *N*,1-bis(6-Methyl-pyridin-3-yl)methanimine as proxy with an imine bond, 6-Methylnicotinaldehyde, and 6-Methylpyridin-3-amine as

model compounds simulating the intercomplex imine formation (Fig. S6). Due to their majority, the N 1s envelope was dominated by contributions from the nitrogen atoms of the terpyridine units. However, in the XPS spectrum of the film made of **2**, a distinct shoulder at higher binding energy was observed, which emerges from imine-type nitrogen species in the film deposited. The quantification of the different nitrogen species was challenging due to the overlap of the peaks of the different nitrogen species. As simple approximation, the recorded peak was simulated as combination of heteroaryl and imine-type nitrogen signals (Figure S6d). Contributions of free amines are in energy in between and contribute comparable to both signals. The integration of the signals (Figure S7) displayed an intensity of the imine-nitrogen peak of about 18% compared with the signal of heteroaryl nitrogen at 82%. For a perfect, periodic chessboard-type 2D polymer, a theoretical fraction of 2/8 (25%) would be expected, suggesting that in the film, about 72% of the terminal amines are engaged in an imine bond. Even so, the quantification of the spectrum is not perfect due to signal overlapping and broadening, and the N 1s profile is in good qualitative agreement with a monolayer-thick and densely packed 2D polymer network, which lacks the intended chessboard-type periodicity, as displayed in Figure 6c).

2.5 | Likelihood of Discrete Oligomers

As already mentioned above, the origin of the increased surface coverage of **2** using optimized casting conditions can't be determined by nc-AFM. As measure of the intrinsic bond forming preference of the structural motive, the theoretical thermodynamic features of well-defined imine-bond-based oligomers were analyzed by Density functional theory (DFT) single point energy calculations at the B3LYP-D3BJ/def2-SVP level using geometries optimized under identical conditions [43]. Even so, these gas-phase electronic energies ignore the complex conditions at the air/water interface, solvent acidity, and entropic contributions, they provide insight about the strain build up by interlinking monomers. Again, bifunctional complex **1** was used as proxy of **2** to minimize the complexity of the potentially formed structures. As sketched in Figure 7, the imine-interlinked structures formed at the air/water interface of the monomer **1** (Figure 7a) are either even-numbered macrocyclic oligomers (Figure 7b) or linear polymers (Figure 7c). Ideal structures to analyze the strain produced by imine interlinking are the macrocycles with all terminal

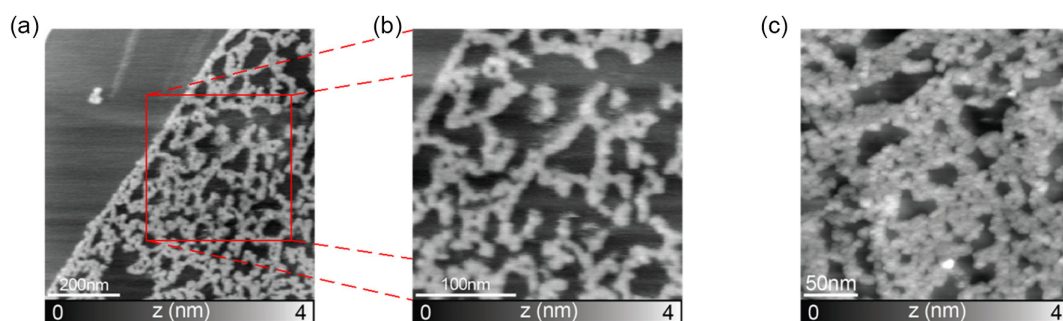


FIGURE 6 | Surface analysis of C_2 -symmetric complex **2**: (a) 1st casting, nc-AFM Topography of a HOPG surface coated at 1 mN m^{-1} in ambient conditions; (b) Zoom in topography of the polymers structures, extracted from (a); (c) nc-AFM topography of 2nd casting at 1.2 mN m^{-1} on HOPG in UHV conditions; Parameters: (a,b) wavemode AF, $A = \text{XX}$; (c) $f_1 = 172 \text{ kHz}$, $A_1 = 4 \text{ nm}$, $\Delta f_1 = -60 \text{ Hz}$.

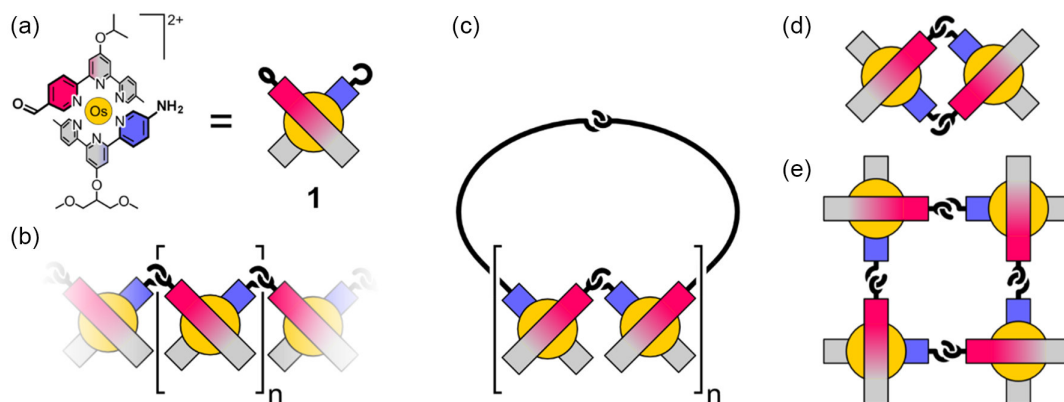


FIGURE 7 | Poly- and oligomers formed upon imine condensation from **1**. (a) monomer; (b) linear oligomer; (c) macrocyclic oligomer; (d) macrocyclic dimer; and (e) macrocyclic tetramer mimicking the desired bond formation in the *LB* experiment.

functional groups engaged in imine bonds. In the macrocyclic dimer ($n=1$ in Figure 7c,d), both reactive sites of one monomer react with the ones of a second monomer, while in the macrocyclic tetramer ($n=2$ in Figure 7c,d), each monomer reacts with two different neighboring monomers. The obtained grid-type tetramer represents a tetrameric subunit of the desired chessboard-type 2D polymer and is thus an interesting model simulating the interlinking properties of the fourfold decorated complex **2**.

For a single monomeric unit (Figure 7a), the calculated total energy was -2434.93 Ha, while the dimer (Figure 7d) gave -4716.93 Ha, and the 2D-arranged tetramer (Figure 7e) resulted in -9432.88 Ha. Normalization per monomer [44] gave very comparable numbers with a slight energetic preference for the circular dimer (-2358.47 Ha per monomer) compared to the 2D-linked tetramer (-2358.22 Ha per monomer). Even so, these values were calculated for conditions far away from the real situation in the *LB*-experiment, the hope was that the tight proximity of the neighboring monomers required to form the macrocyclic dimer (Figure 7d) handicaps this macrocyclic oligomer compared with the tetramer (Figure 7e). However, the values rather suggest that small, locally closed dimeric structures are intrinsically favored over more extended tetrameric structures.

Extrapolating this finding to the polymer formation of **2**, the lack of selectivity between dimer-type and tetramer-type oligomers results in a rich variety of imine-interlinked structures. If the formation of the first of the four possible imine bonds equally likely triggers the formation of the desired tetrameric tile with neighboring monomers as it favors the closure of the neighboring reactive site with the already attached neighbor, both motives are expected in the molecular film. In Figure 8b, a sketch of the resulting network is displayed comprising both the desired tile-type tetramers as well as helical plait-pattern type linear strands. In combination with the considerable number of functional groups that did not form an imine, substantial cross-linking in the molecular film is expected. Such locally compact structures, promoted by preorganization or positive cooperativity of the first formed bond, are a widely established concept [45–48]. As a consequence, once one imine bond is formed, intramolecular formation of a second bond between the same two monomer units may be favored due to their close proximity, biasing early growth toward linear, plait-pattern-type chains. In contrast, formation of 2D-crosslinked polymers requires additional intermolecular reactions with additional monomers. As imine bonds are dynamic, self-sorting toward more stable structures can occur under near-equilibrium conditions [28]. Whether such self-sorting is predominantly under thermodynamic or kinetic control depends on the

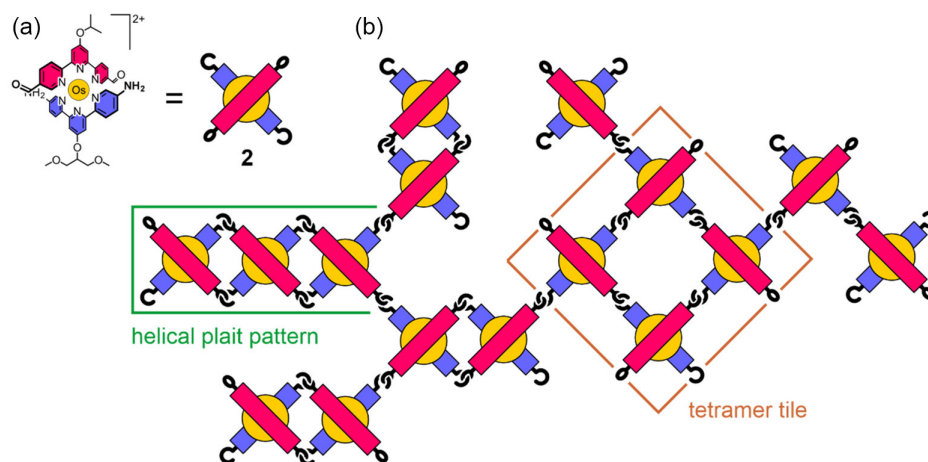


FIGURE 8 | Variety of motives from the imine formation of the tetrafunctional monomer **2**. (a) Structure of the monomer and (b) sketch of a network comprising the motives “helical plait pattern” and “Tetramer tile” which seem to have comparable thermodynamic stabilities.

reaction environment [49]. However, with the minute difference between both motives suggested by theory, the thermodynamic driving force toward the ordered, periodic chessboard-type 2D polymer is missing.

In the nc-AFM images, films cast from the more acidic subphase predominantly show linear, chain-like assemblies formed through intramolecular reactions. When casting from less acidic conditions and transferred from higher surface pressure, the observed polymer shows a higher degree of surface coverage, most likely due to crosslinking formed by intermolecular reactions. We therefore propose that chain formation is both slightly thermodynamically preferred and kinetically favored through intramolecular reactions under more acidic conditions. In contrast, 2D interlinking through intermolecular reactions becomes more accessible under less acidic conditions and higher proximity, consistent with more effective self-sorting under near-equilibrium conditions.

3 | Conclusion

Two amphiphilic heteroleptic osmium complexes were designed and synthesized, and their behavior at the air/water interface was investigated. Both complexes formed stable monolayers that were successfully transferred onto HOPG samples and characterized by AFM techniques. The bifunctional complex **1** produced discrete oligomeric aggregates, whereas the C_2 -symmetric complex **2**, with four imine-forming functionalities, yielded extended, chain-like, and partially interconnected polymeric regions, whose surface coverage improved under optimized interfacial conditions. The lower subphase pH in the polymerization of **2** led to more chain formation, which is in line with the more rapid imine formation due to catalysis and therefore formation of the kinetic product, a result of intramolecular reactions. Rather neutral pH and higher compression led to higher surface coverage. While this can be due to simply compressed linear chains, it can be also indicative of a more crosslinked polymer. Formation of the crosslinked product may be favored through intermolecular reactions providing self-sorting at near-equilibrium conditions when the monomers are in close proximity. While the resulting networks are not long-range-ordered, they nevertheless exhibit clear signatures of lateral polymer growth and possible local interweaving, representing a significant step toward well-defined 2D coordination polymers formed at soft interfaces. XPS data supports the presence of polymeric structures of **2** on the surface and is indicative of imine bond formation.

Overall, this work demonstrates that combining metal-templated preorganization with dynamic imine condensation enables directional growth of polymeric networks under mild interfacial conditions. The findings provide valuable insights into how molecular architecture and interfacial confinement cooperate to guide two-dimensional assembly and thus offer a foundation for the future design of more ordered and densely interconnected coordination frameworks. In this context, the limited long-range order and incomplete surface coverage observed here point to clear design parameters for further optimization. In particular, monomer design may be tuned to disfavor a second intramolecular bond closure and promote

intermolecular cross-linking, for instance, by increasing steric demand or geometric constraint around the reactive sites, biasing the system toward laterally extended polymer growth. In parallel, more detailed structural characterization of the dense polymer regions, including differentiation between chain-like and laterally interconnected motifs, will be required to better correlate molecular design with resulting morphology. Once robust conditions for stable polymerization with high surface coverage are established, interwoven metal-organic polymers can be obtained reliably. At this point, the replacement of osmium by a more labile metal center becomes a promising strategy, hopefully enabling metal removal from the interwoven polymer, accessing fully organic, mechanically interlocked polymeric architectures derived from the metal-organic network preorganized at the air/water interface.

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Conflicts of Interest

The authors declare no conflicts of interest.

Data Availability Statement

The data that support the findings of this study are available in the Supporting Information of this article.

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Supporting Information

Additional supporting information can be found online in the Supporting Information section. Additional supporting information, such as the synthesis procedures of all compounds, their corresponding full characterization, XPS measurements, and more information about the AFM measurements, are provided online in the supporting information. The authors have cited the references [39, 43, 50–57] in the supporting information.