Graphical abstract

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Toward step-by-step nuclear growth of surface two-dimensional porphyrin nanonetworks

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Abstract

We report the development of a solution-based step-by-step technique, which utilizes the coordination bond between metalloporphyrin molecular units and metal linkages and results in the nuclear growth of nano-networks on solid substrates. The growth of the surface structures is strongly influenced by the choice of substrate materials and solvents: the molecule-substrate interaction and the solubility of the molecular units are important parameters in tuning the size and growth of the domains.

Keywords

Interfacial processes; Nanomaterials; Metal-organic frameworks; Molecular assembly;

Solution process

1. Introduction

Development of rational and facile methods for creating ordered structures with nanometer scale precision is one of the central issues in the fields of nanoscience and nanotechnology. Bottom-up approaches utilizing self-assembly processes of molecular systems allow the simple and quick formation of supramolecular structures on surfaces [1-8]. Using suitable designs and choices of molecular building blocks, a variety of surface nanoarchitectures can be prepared – these can be tuned and specific structural motifs can be stabilized by either covalent [9], coordination [10-20], and hydrogen bonds [21,22], or by π - π [23,24] and van der Waals interactions [24-26]. Metal-organic coordination architectures provide further diverse types of ordered structures with one-dimensional (1D, chain), two-dimensional (2D, monolayers) or three-dimensional (3D, multilayers) arrangement as well as attractive chemical-physical properties, such as redox change, catalytic activity and magnetism derived from the metal ion components.

A number of 2D networks of molecular building blocks connected by coordination bonds have been constructed on solid surfaces by both ultra-high vacuum (UHV) techniques and solution-based methods and they have been well-authenticated by scanning microscopy [9-14,21-31]. Surface assemblies fabricated by solution-based processes are more attractive from the point of view of developing realistic candidates for device application because they maintain their ordered arrangement under ambient working conditions [15-20,29-31]. In addition, the preparative protocols can be usually performed with simple inexpensive glass tools and facile reproducible chemical laboratory processes – that is, the primary molecular components and secondary building units (metal ion linkers) are prepared in solution and typically the solution is dropped on the substrate surfaces or the substrate itself is immersed into the solution. A successive step-by-step immersion procedure – alternate dipping of substrates into molecular building block and metal ion solutions accompanied by in-between

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2 rinsing and drying processes – provides well-ordered multilayers including extended porous
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4 assemblies (so called metal-organic frameworks, MOFs or porous coordination polymers,
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6 PCPs) on surfaces [15-20,32-34].
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10 Recently, we have developed a new solution-based methodology in our quest to
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12 construct surface MOF (or PCP) nanoarchitectures with high crystalline order in both the in-
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14 plane and out-of-plane directions to the substrate [15-20]. The technique involves the
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16 combined sequential use of the Langmuir-Blodgett (LB) method [35-40] (this allows us to
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18 exercise superb control of the nanofilm crystallinity in the horizontal direction and to
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20 fabricate well-ordered monolayers on liquid surfaces that can be deposited onto solid
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22 substrates) and the layer-by-layer (LbL) growth method (this provides excellent control of
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24 the film orientation and the number of layers in the vertical direction to the substrate). The
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26 power of the integrated LB-LbL methodology was demonstrated by employing
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28 metalloporphyrin building units and metal ion joints to fabricate for the first time a perfectly
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30 crystalline surface MOF nanofilm. Porphyrins including metalloporphyrins are excellent
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32 candidates as molecular building blocks for the construction of both 2D and 3D
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34 architectures as they are characterized by an approximate two-dimensional (2D) square
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36 planar geometry [39-42]. The existence of a rich variety of (metallo)porphyrin derivatives,
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38 incorporating different center-coordinated metals (or void) and functional group substituents
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40 in the periphery of the molecules, such as pyridine or carboxylate ions, allows a fine control
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42 of the potential linkage motifs in coordination-bond-driven array fabrication both in the bulk
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44 crystalline state and at the nanoscale level, as demonstrated by the LB-LbL method [15-18].
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54 As the dimensions of nanosized objects strongly influence their chemical and physical
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56 properties [45-50], fine control of the domain size of the surface nanostructures both
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58 laterally and vertically is an important target to address. The layer-by-layer (LbL) film
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60 growth strategy used above is an invaluable tool towards achieving the goal of generating
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2 surface crystalline multilayer assemblies of any desired thickness at the nanometer scale (*i.e.*
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4 with controlled domain size in the vertical direction). However, although the LB fabrication
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6 component of our earlier methodology obviously ensures the construction of well-crystalline
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8 monolayers, the assembly of surface 2D nanoarchitectures with completely controlled
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10 domain size at the sub-monolayer level in the film orientation parallel to the substrate
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12 surface has not been developed as yet.
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17 In this paper, we demonstrate how a successive step-by-step immersion procedure
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19 can be applied to allow fabrication of metal-directed surface nanostructures consisting of
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21 metalloporphyrin molecular units. The developed experimental process is based on the idea
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23 of nuclear growth, which has been applied to the controlled synthesis of oligomeric
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25 suprastructures. Optimization of the fabrication conditions together with appropriate
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27 selection of the molecular building units and substrates employed have allowed us to guide
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29 the growth of nanostructured films in the direction parallel to the substrate.
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37 **2. Experimental**

38 *2.1. Materials and measurements*

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42 5,10,15,20-Tetra(4-pyridyl)-porphine zinc (II) (ZnTPyP) (purity 90%) was purchased
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44 from Porphyrin Systems. *Trans*-bis(benzonitrile)dichloropalladium (II) ($\text{PdCl}_2(\text{NCPh})_2$)
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46 (99.99%) was purchased from Alfa Aesar. Pure grades of chloroform and methanol were
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48 purchased from Wako Pure Chemical Industries Ltd. or Junsei Chemical Co. Ltd. All
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50 chemicals were used as received without further treatment.
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55 Three different solid substrates were employed for deposition and growth of the 2D
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57 submonolayer molecular arrays: (i) Au substrate (Au/Cr/ITO/glass): indium tin oxide (ITO)
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59 ($3000 \text{ \AA} \pm 10\%$), chromium ($50\sim 100 \text{ \AA}$) and gold (99.99%, $100 \text{ \AA} \pm 10\%$) were deposited
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61 successively under high vacuum onto glass plates at GEOMATEC Corporation. (ii) Quartz
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substrates: these were purchased ($20 \times 25 \text{ mm}^2$, 0.5 mm thickness) from SEIKO Co. Ltd. (iii) Sapphire ($\alpha\text{-Al}_2\text{O}_3$ single crystal) substrates: the sapphire (0001) surface was annealed with a hydrogen flame which created a uniform step structure with a terrace width of about 100 nm and a step height of 0.2 nm, attributed to the monolayer height of $\alpha\text{-Al}_2\text{O}_3$. The off-angle was 0.15° . All substrates were immersed into an ultrasonic bath of chloroform and methanol, and then dried before the film fabrication.

UV-visible absorption spectra of the solutions and the films fabricated on Au/Cr/ITO/glass, quartz and sapphire substrates (*vide infra*) were measured in transmission mode with a Jasco V-570 spectrophotometer at room temperature. In the solution UV-vis spectroscopy measurements, 15 μL of a 10 μM $\text{PdCl}_2(\text{NCPh})_2$ solution in chloroform was titrated into a quartz cell containing 3 mL of a 0.5 μM ZnTPyP chloroform/methanol (3:1, v/v) solution (1.5 nmol) and stirred for 10 minutes at room temperature. The titration was repeated eight times and the total amount of added $\text{PdCl}_2(\text{NCPh})_2$ was 12 nmol.

2.2. Fabrication of nanoarrays on solid substrates

The 2D ZnTPyP-Pd arrays were deposited on the solid substrates and control of their domain size was attempted by repeated step-by-step growth protocols that included sequential reagent deposition, intermediate rinsing/solvent immersion and drying steps. The experimental procedures for the two growth protocols employed in this work are collected in Table 1.

TABLE 1. Summary of the experimental procedures employed in the two protocols of 2D ZnTPyP-Pd array fabrication on solid substrates.

	Protocol I	Protocol II
Process #1 ZnTPyP deposition	10 μ M ZnTPyP in CHCl ₃ /CH ₃ OH, 5 sec	10 μ M ZnTPyP in CHCl ₃ /CH ₃ OH, 5 sec
Process #2 Rinsing	CHCl ₃ , 5 sec	CHCl ₃ /CH ₃ OH, 10 sec
Process #3 PdCl ₂ (NCPPh) ₂ deposition	10 μ M PdCl ₂ (NCPPh) ₂ in CHCl ₃ , 1 min	10 μ M PdCl ₂ (NCPPh) ₂ in CHCl ₃ , 1 min
Process #4 Rinsing	CHCl ₃ , 5 sec	CH ₃ OH, 10 sec, followed by CHCl ₃ /CH ₃ OH, 10 sec

Protocol I: Each substrate was first immersed into a 10 μ M ZnTPyP chloroform/methanol (3:1, v/v) solution for 5 sec (process #1). This was followed by immersion into chloroform for 5 sec, and drying by nitrogen blowing (process #2). Then the substrate was immersed into a 10 μ M PdCl₂(NCPPh)₂ chloroform solution for 1 min (process #3). This was again followed by immersion into chloroform for 5 sec, and finally drying by nitrogen blowing (process #4). The growth of the resulting Pd-mediated ZnTPyP arrays (ZnTPyP-Pd) is controlled by the number of deposition cycles (processes #1~#4). For comparison, for each substrate treated with the procedures described by protocol I above, an additional substrate was also prepared using the same number of cycles as before but omitting processes #3 and #4 (*i.e.* omitting the PdCl₂(NCPPh)₂ deposition steps).

Protocol II: This involved a modified procedure to the experimental processes adopted in protocol I above. While the two reactant solution (ZnTPyP and PdCl₂(NCPPh)₂) immersion steps (#1 and #3) were kept the same, the solvent rinsing procedures (#2 and #4) were extended and the solvents involved were changed. Process #2 now involved immersion into a mixture of chloroform/methanol (3:1, v/v) for 10 sec, and drying by

nitrogen blowing (process #2). Similarly, process #4 first included dipping into methanol for 10 sec followed by dipping into a mixture of chloroform/methanol (3:1, v/v) for 10 sec successively, and finally drying by nitrogen blowing. Processes #1~#4 were similarly repeated to change the size of the resulting 2D ZnTPyP-Pd domains. Control substrates were prepared for comparison by omitting their dipping into the Pd-containing solutions (processes #3 and #4).

3. Results and Discussion

3.1. Materials selection and strategy

Our experimental strategy for the fabrication of 2D arrays with well-controlled domain size on solid surfaces at the molecular scale is to first deposit single molecular units which can act as nuclear centers from which multi-molecular arrays can be grown by attaching additional molecules through suitable metal ion linkers. The fabrication process includes immersion of the solid substrate into a molecular building unit solution and a metal ion linker solution in an alternating fashion – this procedure is comparable to that employed in LbL growth protocols. However, selection of the molecular unit, substrate, solvent and reaction conditions (immersion time and solution concentration) is here of key importance to allow control of the lateral domain size instead of the vertical film growth resulting from the LbL deposition technique.

Porphyrin molecules are ideal molecular building units to be integrated in 2D nuclear growth strategies. Their 2D square-planar geometry usually leads them to lie with the molecular plane preferentially parallel to the surfaces. In order to further enhance this general directional tendency, we chose here a tetratopic pyridine-substituted metalloporphyrin, ZnTPyP, because the preferred alignment direction of the pyridine units is also parallel to the surfaces – this together with the linear coordination metal linkers,

trans-PdCl₂(NPh)₂ effectively guides additional molecules to connect in a restricted direction manner [51-53]. Using solvents in which the molecular system is very soluble (highly concentrated solutions) and if the interactions between molecules and substrates are weak, this may result in no adsorption of molecules to the substrate surface. On the other hand, the inverse set of conditions (very dilute solutions, strong molecule-substrate interactions) may cause the creation of many molecular nuclei strongly attached onto the surface, thereby preventing the growth of the array to the desired size. The optimum fabrication condition should be to provide a small number of molecular nuclear seeds, which have the freedom to rotate and move on the substrate surface. Immersion of the substrate after the deposition of the ZnTPyP molecules into the metal linker PdCl₂(NPh)₂ solution (Process #3) can lead to coordinative bridging between the peripheral pyridine substituent parts of the metalloporphyrin and palladium, resulting in the growth of the ZnTPyP assemblies. The subsequent rinsing process eliminates any unreacted metal linkers and ZnTPyP molecules deposited on the substrate surface (Process #4). Repetitive cycles of the step-by-step deposition and rinsing protocols may lead to the generation of 2D molecular assemblies of desired domain size.

The reaction between ZnTPyP and PdCl₂(NPh)₂ in the solution state was first investigated by UV-vis absorption spectroscopy. Titration of PdCl₂(NPh)₂ solution into ZnTPyP solution results in substantial broadening, a concomitant decrease in intensity, and a red shift of the Soret band, as shown in Fig. 1. These experimental observations are typically encountered in electronically coupled porphyrins and, for instance, are observed for Pd-mediated dimer, tetramer, and square porphyrin arrays [51-53].

Fig. 1. UV-vis absorption spectra of ZnTPyP solution upon titration with $\text{PdCl}_2(\text{NCPh})_2$ solution – a substantial broadening, a concomitant decrease in intensity and a red shift of the Soret band are observed.

3.2. Nuclear growth of nanoarrays using protocol I

We first initiated our search for appropriate growth conditions by applying protocol I to two different substrates, quartz and Au. Deposition of ZnTPyP molecules on the substrate surface was followed by UV-vis absorption spectroscopy. Figures 2a and 3a show the Soret band of ZnTPyP for each cycle of the alternate quartz (Fig. 2a) and Au (Fig. 3a) substrate immersion into ZnTPyP and $\text{PdCl}_2(\text{NCPh})_2$ solutions followed by the rinsing procedure (process #1 ~ #4). Dashed and solid lines in Fig. 2a, 2b, and 3b represent the spectra obtained before and after the immersion process into $\text{PdCl}_2(\text{NCPh})_2$ solution, respectively. For comparison, absorption spectra for each cycle without immersion into $\text{PdCl}_2(\text{NCPh})_2$ solution were also collected (Fig. 2c and 3c).

Fig. 2. UV-vis absorption spectra of ZnTPyP-Pd arrays deposited on a quartz substrate using protocol I. (a) The Soret band of ZnTPyP after successive cycles of alternate substrate immersion into ZnTPyP and $\text{PdCl}_2(\text{NCPh})_2$ solutions – each spectrum is labeled by the corresponding cycle number (1–10). (b) The Soret band of ZnTPyP after three growth cycles. Dashed and solid lines in (a) and (b) show the spectra measured before and after the immersion process into the $\text{PdCl}_2(\text{NCPh})_2$ solution, respectively. (c) The Soret band of ZnTPyP after successive cycles of substrate immersion into ZnTPyP solution but without immersion into $\text{PdCl}_2(\text{NCPh})_2$ solution. (d) Maximum absorbance of the ZnTPyP Soret band *versus* the number of deposition cycles in (a) and (c).

Fig. 3. UV-vis absorption spectra of ZnTPyP-Pd arrays deposited on an Au substrate using protocol I. (a) The Soret band of ZnTPyP after successive cycles of alternate substrate immersion into ZnTPyP and $\text{PdCl}_2(\text{NCPh})_2$ solutions – each spectrum is labeled by the corresponding cycle number (1–10). (b) The Soret band of ZnTPyP after three growth cycles. Dashed and solid lines show the spectra measured before and after the immersion process into the $\text{PdCl}_2(\text{NCPh})_2$ solution, respectively. (c) The Soret band of ZnTPyP after successive cycles of substrate immersion into ZnTPyP solution but without immersion into $\text{PdCl}_2(\text{NCPh})_2$ solution. (d) Maximum absorbance of the ZnTPyP Soret band *versus* the number of deposition cycles in (a) and (c). The horizontal line marks the calculated maximum absorbance for a ZnTPyP-Pd monolayer with 100% surface coverage estimated by taking into account the molar absorption coefficient of ZnTPyP and the number of molecules present after considering the molecular orientation relative to the substrate surface as shown in Fig. S1.

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7 The red shift in the Soret band of ZnTPyP observed after the $\text{PdCl}_2(\text{NCPh})_2$
8 immersion in each cycle (Fig. 2a, 2b, and 3b) shows that the $\text{PdCl}_2(\text{NCPh})_2$ -linked ZnTPyP
9 molecules interact strongly enough for the electronic state to change. A continuous increase
10 in absorbance with increasing number of cycles is observed for both substrates, while in the
11 absence of $\text{PdCl}_2(\text{NCPh})_2$ immersion, the absorbance saturates after only the second cycle
12 of the deposition process (Fig. 2c and 3c). This implies that the immersion step into the
13 $\text{PdCl}_2(\text{NCPh})_2$ solution is necessary for successful ZnTPyP deposition and therefore, the
14 growth of ZnTPyP arrays proceeds together with Pd intermediation. The small increase in
15 absorbance observed up to the third cycle in the case of the gold substrate even without the
16 $\text{PdCl}_2(\text{NCPh})_2$ immersion step (Fig. 3c) might be attributed to further deposition of ZnTPyP
17 molecules on void parts of the substrate surface. Saturation of absorbance toward the
18 calculated value for a monolayer implies that the deposition completes when the surface is
19 fully covered by ZnTPyP molecules and further immersion and rinse cycles do not cause
20 any growth of the arrays. Furthermore, the continuous red shift of the ZnTPyP Soret band
21 with increasing number of deposition cycles (Fig. 2a and 3a) is consistent with the
22 additional ZnTPyP molecules adsorbed in the repetitive deposition cycles being
23 electronically connected to other as-deposited molecules on the substrate surface, thereby
24 leading to successful step-by-step growth of the arrays.

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51 The arrays grown in this way are poorly soluble into the solvents employed so that
52 they can remain on the surface even after rinsing. On the other hand, as-deposited
53 uncoordinated ZnTPyP molecules on the substrate without $\text{PdCl}_2(\text{NCPh})_2$ intermediation
54 are removed from the surface at each rinsing process because ZnTPyP easily dissolves in
55 chloroform/methanol (Fig. 2c and 3c).
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Finally, we note that the absorbance measured after deposition on an Au substrate is more intense than that for quartz substrates for all deposition cycles (Fig. 4). Therefore, we consider that the interaction between the deposited ZnTPyP molecules and Au is stronger than that between ZnTPyP and quartz – this leads to a larger number of ZnTPyP molecules adsorbed on the Au surface, while at the same time it results in fewer molecules being removed by rinsing with the solvent. This is also consistent with the intense absorbance observed for Au surface deposition without $\text{PdCl}_2(\text{NCPh})_2$ immersion (Fig. 3d) and the comparable value between the measured absorbance and that calculated for a monolayer film indicating that ZnTPyP can be deposited on Au without Pd intermediation. Furthermore, the absorbance of ZnTPyP arrays on the Au substrate increases linearly, while the one measured for the quartz substrate deposition grows exponentially (Fig. 4). This implies that in the case of the quartz substrate each nuclear ZnTPyP molecule allows several molecules to attach around resulting in a non-linear increase of the absorbance.

Fig. 4. Comparison of the change in maximum absorbance of ZnTPyP-Pd arrays on quartz and gold substrates with number of deposition cycles using protocol I. The absorbance is larger for Au than that for quartz substrates for all deposition cycles.

3.3. Nuclear growth of nanoarrays using protocol II

The growth of the 2D arrays depends critically on the number of nuclear molecules present on the same surface. Smaller numbers of nuclear molecules deposited on the substrate should allow the creation of bigger size arrays, while larger numbers prevent individual array growth. The fabrication process was therefore modified to make use of this idea and 2D ZnTPyP arrays were deposited on quartz substrates using protocol II (see experimental section, Fig. 5). The mixed chloroform/ methanol solvent (in which ZnTPyP is more soluble) and the additional step of methanol immersion (in which $\text{PdCl}_2(\text{NCPH})_2$ is very soluble) were introduced in the rinsing processes (process #2 and #4) of protocol II, so that unreacted starting molecules, which may be present in the course of nuclear growth, can be effectively removed. Continuous increase in absorbance with repetition cycles was observed in the ZnTPyP assemblies prepared by protocol II and the absorbance changes with the number of cycles for both protocols I and II are summarized in Fig. 6. A reduced value of the absorbance of the Soret band in each cycle was observed for the arrays fabricated on quartz substrates with protocol II. This shows that we indeed succeeded in depositing a smaller number of nuclear molecules on the substrate surface and that unreacted starting materials were effectively removed with protocol II. Moreover, in contrast to the situation encountered in the protocol I experiments, the values of the absorbance for the arrays fabricated with protocol II display a clear tendency to saturate

with increasing number of cycles (Fig. 6) towards the absorbance value calculated for a monolayer when considering explicitly the molecular arrangement of the film. This clearly implies termination of the nuclear growth process with increasing number of deposition cycles at the monolayer stage and shows the success of our modified growth strategy (protocol II) in achieving larger size arrays by restricting the number of initial nuclear molecules present.

Fig. 5. UV-vis absorption spectra of ZnTPyP-Pd arrays deposited on a quartz substrate using protocol II. (a) The Soret band of ZnTPyP after successive cycles of alternate substrate immersion into ZnTPyP and $\text{PdCl}_2(\text{NPh})_2$ solutions – each spectrum is labeled by the corresponding cycle number (1–11). (b) The Soret band of ZnTPyP after four growth cycles. Dashed and solid lines in (a) and (b) show the spectra measured before and after the immersion process into the $\text{PdCl}_2(\text{NPh})_2$ solution, respectively.

Fig. 6. Maximum absorbance of the ZnTPyP-Pd Soret band *versus* the number of deposition cycles for arrays fabricated on quartz substrates using protocols I and II. A reduced value of the absorbance in each cycle is observed for the protocol II arrays. This shows that using protocol II we succeeded in depositing a smaller number of nuclear molecules on the substrate surface and in effectively removing unreacted starting materials.

In order to investigate the surface morphology of the ZnTPyP arrays, we also applied the protocol II array fabrication technique to suitable substrates which can be used to observe molecular-scale surface objects by the AFM technique. Atomically flat sapphire was chosen as such a substrate and the deposition of ZnTPyP molecules on the substrate surface and the 2D array growth were first followed by UV-vis absorption spectroscopy (Fig. S2). Figure 7 shows the AFM images of the molecular arrays and the bare sapphire surface. The cross section for the ZnTPyP arrays exhibits a slightly higher part (~0.6 nm)

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2 than the other domains (~0.4 nm). The existence of the high part might be attributed to a
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4 minority of ZnTPyP molecules tilting away from the substrate surface when deposited at
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6 the edge of the sapphire surface steps or on top of other ZnTPyP molecules and are not
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8 removed by the rinsing process. Domains with 20-40 nm size were observed in the images
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10 of the ZnTPyP arrays (Fig. 7a), while step structures with about 100 nm width were
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12 observed for the sapphire substrate (Fig. 7b). As the optical spectroscopy results have
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14 established that the domain size grows with increasing number of cycles, we can obtain a
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16 rough estimate of the size of each domain in the nuclear growth method as: domain size $\approx$
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18 $\{1+([\text{cycle number}]-1)\times 2\}\times[\text{molecular size}]$. Considering that the average size of the
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20 repeat ZnTPyP-Pd molecular units in the 2D arrays ranges between about 2.1 nm (shortest
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22 part) and 3.0 nm (longest part) and that the number of cycles for the present film is six, the
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24 estimated domain size of the arrays is: $\{1+(6-1)\times 2\}\times(2.1\sim 3.0) \text{ nm} \approx 23\sim 33 \text{ nm}$. This is in
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26 excellent agreement with the observed domain size of 20-40 nm, providing good support
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28 for the successful demonstration of our surface nuclear growth strategy of the molecular
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30 assembly linked by metal joints with well-optimized step-by-step deposition protocols.
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Fig. 7. Surface morphology of the ZnTPyP-Pd arrays prepared on an atomically flat sapphire substrate. (a) AFM height image (top) and cross section (bottom) of the ZnTPyP-Pd arrays after six repetition cycles using protocol II. (b) AFM height image of the bare sapphire surface. The size of domains observed in the images of the ZnTPyP-Pd arrays is 20-40 nm, while step structures of about 100 nm width are observed for the sapphire substrate.

4. Conclusions

In this work, we have demonstrated the solution-based step-by-step growth of nano-assemblies on solid surfaces utilizing coordinative bond linkage. Our approach to fabricate 2D surface arrays is based on a nuclear growth method. Instead of allowing the molecular building blocks to react with metal ion linkers and the domain size of the product to grow freely as employed in solvothermal crystal synthesis, we developed a methodology of

1
2 applying alternating immersion of the substrate into two reactant solutions together with
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4 intermediate rinse processes: we first deposit single isolated molecular units that can act as
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6 nuclear centers from which multi-molecular arrays can then be grown by attaching
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8 additional molecules through suitable metal ion linkers. The array growth was monitored
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10 by UV-vis spectroscopy. We are currently exploring the versatility of the growth technique
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12 as applied to various molecular units and metal ion linkers and are examining the influence
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14 of the finely controlled surface structure to chemical/physical properties such as thermal
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16 stabilities and electronic/optical characteristics.
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