1 Preparing macromolecular systems on

surfaces: general discussion

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Sebastian Schwaminger, Johannes Seibel, Steven Tait, Joan Teyssandier

and Han Zuilhof

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(400:[400]400) Karl-Heinz Ernst opened a general discussion of the paper by

Lifeng Chi: I was a little surprised at how high in temperature you have to go for

this deoxygenation. Ullmann coupling is normally around 200 oC. Why do you

need a higher temperature? Is it because of dehalogenation?

Lifeng Chi replied: Decarboxygenation seems to be more difficult than

dehalogenation.

(401:[401]401) Karl-Heinz Ernst asked: Does this reaction (decarboxygenation)

also work on gold?

Lifeng Chi answered: No, it does not work on gold, also not on silver.

(402:[402]402) Claire-Marie Pradier commented: At high temperature, don’t

you have dehydrogenation of the molecules?

Lifeng Chi responded: From our experience, I believe that hydrogenation

should take place. This might be the reason why it is not easy to increase the yield

for obtaining graphene nanoribbons.

(403:[403]403) Peter Beton commented: Following on from the last question,

have you tried with perylene itself (rather than PTCDA)?

Lifeng Chi replied: We have not tried perylene yet. It could be an interesting

system to study.

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(404:[404]404) Philip Davies asked: In gure 4, aer you’ve exposed it to oxygen

at 470 K, there are patches on the surface apparently bound by perylene chains.

Are those areas where the surface has oxidised? Is it that the perylene chains are

conning the area of oxidation, or are they organising themselves so that they

bind to the edges of the areas where there’s oxidation?

Lifeng Chi answered: The patches are oxidized areas. Although other empty

areas (not occupied by the perylene chains) could be oxidized too (see the ESI for

our paper, DOI: 10.1039/C7FD00129K), those patches conned by the perylene

chains are apparently higher. This may hint that the conned areas are easier to

oxidize. This phenomenon needs to be further investigated.

(405:[405]405) Joan Teyssandier asked: What happens in terms of structures

formed and reaction efficiency if you anneal at a higher temperature than 630 K?

In particular, have you ever observed any lateral fusion of graphene nanoribbons

on Cu like it has been seen on Au and Ag?

Lifeng Chi replied: Because we already have a more disordered structure at 630

K, probably due to the dehydrogenation, we did not try to further increase the

annealing temperature.

(407:[407]407) Claire-Marie Pradier queried: In the absence of oxygen, what is

the effect of possible defects, steps, etc. on the pristine surface with which you’re

working, on the alignment of your ribbons?

Lifeng Chi responded: Step edges surely help with the alignment of the

ribbons. From our experience, high index crystal surfaces are even better.

(408:[408]408) Rasmita Raval commented: The organometallic linked species

you show all have good registry with the underlying surface. However, this registry

is lost in the C–C coupled systems you showed. We see the same type of behaviour.

1 Do you think the C–C coupled polymers have a much weaker interaction

with the surface?

1 S. Haq et al., ACS Nano, 2014, 8, 8856.

Lifeng Chi responded: Compared to the metal coordinated organic complexes,

I think that the C–C polymers have weaker interactions with the surfaces. But for

aromatic polymers, the interaction cannot be too weak.

(410:[410]410) Steven Tait asked: At the high temperatures used in your

studies, it seems likely that there would be some dehydrogenation, as has been

observed in other systems on copper surfaces.1 Do you think it is possible that

some of the disorder in the systems aer high temperature treatment is due to

dehydrogenation and C–Cu bond formation (chemisorption) that would prevent

the adsorbates from diffusion and re-ordering and thereby lead to a more

disordered structure?

1 C. G. Williams, M. Wang, D. Skomski, C. D. Tempas, L. L. Kesmodel and S. L. Tait, Surface

Science, 2016, 653, 130–137.

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Lifeng Chi replied: Absolutely. We think that the hydrogenation and the

uncontrolled C–C coupling is the main reason for the disorder. In fact this is the

reason we tried the oxidation, in order to lower the temperature for the C–Cu

bond in the metal-organo chains.

(412:[412]412) Nerea Bilbao queried: If I understood correctly, you are looking

for ways to weaken this C–Cu bond in the reaction intermediate. I was wondering

if you had tried to decouple the molecular structure from the surface, by intercalation

of atoms or small molecules? For instance, iodine atoms can be intercalated

between the metal surface and the organic product, as shown by the group

of Prof. Markus Lackinger in their recently published work.1 They report the

successful post-synthetic decoupling of covalent polyphenylene networks from

a Au(111) surface by intercalation of a chemisorbed iodine monolayer. Another

relevant example was also published this year by Deniz et al.. In this work, they

intercalate in situ Si to suppress the strong contribution of the Au(111) surface

state. Their rst-principles calculations provide insight into substrate induced

screening effects, which result in a width-dependent band gap reduction for

substrate-supported AGNRs.

1 A. Rastgoo-Lahrood et al., 2017, Nanoscale, 9, 4995.

2 O. Deniz et al., Nano Lett, 2017, 17, 2197–2203.

Lifeng Chi answered: Thanks for the suggestion. We have not yet tried

decoupling by introducing other atoms or small molecules (except oxygen). We

may try this in future work.

(413:[413]413) Steven De Feyter asked: I’m not so familiar with this copper

oxidation process that can take place, but it seems to be conned in space by areas

dened by the adsorbed polymers. Is it of interest to learn more about the copper

oxidation process itself?

Lifeng Chi answered: It should be an interesting issue to follow. It could be

related to oxygen diffusion on the surface, but this is not conrmed yet.

(414:[414]414) Claire-Marie Pradier asked: If I understood correctly, the oxygen

is added aer the formation? What is this for? And what were you expecting from

using reducing gases?

Lifeng Chi replied: Yes, oxygen is added aer the formation of the perylene–Cu

complex. The aim is to oxidize the Cu which may help to break the Cu–C bond

more easily. Reducing gas is used mainly as the control experiment.

(415:[415]415) David Amabilino commented: Very nice talk. Following on from

the last point, from the work we did with Rasmita Raval and others, when you

have this cuprate bound to the surface it is tremendously stable. It is interesting

that your surface reacts faster than the cuprate (in solution, these compounds are

quite reactive). Are we missing something here? Chemically, that’s really interesting.

You’d think they would be more reactive. Could that chemical architecture

be interesting for something, what possibilities do you see?

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Lifeng Chi responded: We are also very interested in such unique cuprate

structures and their stability against temperature, even in oxygen. We are going to

explore the catalytic activities of such structure, both from experimental and

theoretical sides. Electrochemical and spectroscopic detection could be suitable

methods to prove their catalytic activities.

(416:[416]416) Steven De Feyter asked: Probably a more general question and

maybe a bit provocative. You synthesize a new material on a copper surface in

ultrahigh vacuum. What are the steps that must be taken to really use such

material, for instance by removing it from copper and transferring it to another

substrate? What are the important steps and how feasible are they?

Lifeng Chi responded: Directly using the structured materials on surfaces

might be a more effective way than to remove them from the surfaces. For

instance, the copper–perylene complex is quite stable against annealing. The

single (or bi-) metal atom (not necessarily copper) might be catalytically active. If

one can directly apply the materials for catalytic use, it will become very attractive.

(419:[419]419) Steven De Feyter opened a general discussion of the paper by

Ahmad Jabbarzadeh: Is the surface that you used structured?

Ahmad Jabbarzadeh replied: As described in the manuscript, all surfaces are

atomically structured. The lattice size of various surfaces can be found in Table 1

in our paper (DOI: 10.1039/C7FD00071E).

(420:[420]420) Steven De Feyter continued: What is the relation between the

orientation of the alkane chains in the crystallizing droplets and the symmetry

axes of the substrate underneath?

Ahmad Jabbarzadeh responded: Figure 8b in our paper (DOI: 10.1039/

C7FD00071E) shows the molecular conguration for the entire lm, and the

attached Fig. 1 shows the molecules in the rst layer immediately next to the

Fig. 1 Molecules in the first later immediately next to the smooth surface

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smooth surface. We can see from both gures, the orientation of the molecules is

random and does not follow any particular lattice symmetry of the underlying

substrate. However, the molecules seem to be mostly parallel with other molecules

in a given domain, where they share a common orientation. Even the

smooth surface has some atomic level corrugation however, since the lattice size

is 0.286 nm and the LJ length parameter of the polymers is s ¼ 0.393 nm, it is less

likely for them to give rise to a directional order to template the underlying crystal.

The smoothness of the surface, on the other hand, is expected to help with

creating a planar order. We know, from previous work with shorter conned

alkanes, that for connement induced order, the planar order depends on both

the smoothness and degree of the corrugation of the underlying substrate.1–5

1 A. Jabbarzadeh, P. Harrowell and R. I. Tanner, Crystal bridges, tetratic order, and elusive

equilibria: The role of structure in lubrication lms, Journal of Physical Chemistry B, 2007,

111, 11354–11365.

2 A. Jabbarzadeh, P. Harrowell and R. I. Tanner, The structural origin of the complex

rheology in thin dodecane lms: Three routes to low friction, Tribology International, 2007,

40, 1574.

3 A. Jabbarzadeh, P. Harrowell and R.I. Tanner, Crystal bridge formation marks the transition

to rigidity in a thin lubrication lm, Physical Review Letters, 2006, 96, 206102.

4 A. Jabbarzadeh, P. Harrowell and R.I. Tanner, Low friction lubrication between amorphous

walls: unravelling the contributions of surface roughness and in-plane disorder, Journal of

Chemical Physics, 2006, 125, 034703.

5 A. Jabbarzadeh, P. Harrowell and R. I. Tanner, The very low friction state of a dodecane lm

conned between mica surfaces, Physical Review Letters, 2005, 94, 126103.

(421:[421]421) Steven De Feyter queried: Does the surface, without the nanostructured

features, template the crystallization in any way?

Ahmad Jabbarzadeh responded: Even the smooth surface has some atomic

level corrugation, however since the lattice size is 0.286 nm and the LJ length

parameter of the polymers is s¼0.393 nm, it is less likely for them to give rise to

a directional order to template the crystal. The smoothness of the surface on the

other hand is expected to help with creating a planar order.

(422:[422]422) Steven De Feyter commented: What is the impact of the initial

size of the alkane droplet on the crystallization process?

Ahmad Jabbarzadeh responded: We have done preliminary studies with an

isolated drop (without surfaces) on the effect of droplet size on crystallization

kinetics. This shows great dependence, and we hope to publish the full results in

the near future. For the droplet on the surface, the droplet size was chosen as such

to ll in the cavities formed by the pillars when the surface is fully wetted by the

droplet. As described in the paper, for such a system, a variety of roughness sizes

are simulated to explore the effect of the roughness size.

(423:[423]423) Sebastian Schwaminger said: You investigated the surface

wetting and the surface structure for the Wenzel case. For the Cassie-Baxter case,

would different wetting behaviour affect the crystallinity of the polymers? And

would these results be different from at surfaces?

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Ahmad Jabbarzadeh replied: We have not simulated the crystallization of

a drop in the Cassie-Baxter state. We would expect different behavior as there will

be less contact with the underlying surface, therefore the crystallization kinetics

will be closer to that of an isolated drop under vacuum.

(424:[424]424) Sebastian Schwaminger asked: Would it be difficult to simulate

the Cassie-Baxter wetting, considering the surface roughness and the lower

interfacial area compared to at surfaces?

Ahmad Jabbarzadeh responded: We already have the congurations for the

Cassie-Baxter state and it will be relatively easy to conduct crystallization simulations

for this case.

(425:[425]425) Sebastian Schwaminger continued: Another question, could you

also think about changing the crystallinity with surface curvature? How would

a convex or concave surface affect the crystallinity of your polymers? Here, the

degree of curvature and the size of the droplet should play a critical role as well.

Ahmad Jabbarzadeh answered: We have not simulated such cases, however we

believe that it will be relevant in the context of surface-liquid interactions and only

important if the radius of curvature of both the droplet and the surface are very

close. In other words, it is only important if the radius of curvature of the surface

is such that the interaction of the liquid-surface is affected.

(429:[429]429) Talat Rahman commented: I’m confused. You start with the

nanoparticle that’s composed of these polymer molecules. There’s some interaction

that holds these molecules together and they form a nanoparticle of

\_15 nm in size, then you drop it on a surface. First, you drop it on a smooth

surface, then you have some Lennard-Jones interaction which couples the

molecules in the nanoparticle with the surface. Then you do your simulation for

various temperatures, and at some point you nd that the nanoparticle breaks

apart?

Ahmad Jabbarzadeh replied: The initial wetting simulations on the smooth

surfaces are all conducted at the same temperature. What makes the nano-drop

spread and break-up on one of the surfaces (a ¼ 0.286 nm), is the stronger

wettability of the surface. The higher wettability is due to the smaller lattice size

(packing more atoms on the same area).

(430:[430]430) Talat Rahman continued: So the role of the surface is through

this Lennard-Jones potential? It has a corrugation. Next you replace that surface

with a rough surface? That roughness is nothing but a vicinal surface of that

crystal instead of Cu(100), is that correct? Or are you saying that you create

a modulation of the surface, producing conned structures which are not related

to vicinal surfaces?

Ahmad Jabbarzadeh answered: The surface atoms, and polymer molecules

interact only through this Lennard-Jones potential. The smooth surface has

corrugation only at the atomic length scale. The underlying atomic crystal

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structure for all the rough surfaces is Fe(100). The roughness is created by cutting

patterns through a crystal Fe slab on the (100) plane. That is akin to machining

a crystalline surface via some precision machining or ablation method. The rough

surfaces create deep connement space for the polymer molecules. I believe this

structure is somehow different to vicinal surfaces where surface steps are rather

shallow.

(431:[431]431) Giovanni Costantini said: The system you are simulating seems

essentially to be a very concentrated, liquid drop of polymers, something that I

might imagine could occur at quite high temperatures. How representative is this

of the actual conditions used in the growth and crystallization of polymeric thin

lms?

Ahmad Jabbarzadeh replied: A representative condition relevant to the simulated

system occurs in the recent development of a variation of PVD (Physical

Vapour Deposition) using matrix assisted pulsed laser evaporation (MAPLE).1 The

MAPLE method is based on additive deposition of nanodroplets of the polymer on

a substrate. Polymeric thin lms are oen deposited by casting from solutions.

Despite this being an easy method, due to the short processing time, there is

limited control of the nucleation and crystallization and eventual morphology of

the polymeric lms. The development of other deposition methods, such MAPLE,

offers more control of the crystallinity and morphology of the deposited lms.

1 Jeong Hyuncheol, Kimberly B. Shepard, Geoffrey E. Purdum, Yunlong Guo, Yueh-Lin Loo,

Craig B. Arnold, and Rodney D. Priestley, Additive growth and crystallization of polymer

lms, Macromolecules, 2016, 49, 2860–2867.

(432:[432]432) Giovanni Costantini commented: A led of research where it’s

absolutely essential to be able to control and modify the crystallinity of polymeric

thin lms, is that of conjugated polymers used in organic electronics and

photovoltaic devices. Would you be able to include the solvent and the conditions

used in spin coating in your simulations? I guess that this might have a high

relevance.

Ahmad Jabbarzadeh answered: It is true that polymeric thin lms are oen

deposited from solutions. Despite this being an easy method, due to short processing

time, there is limited control of the nucleation and crystallization and

eventual morphology of the polymeric lms. We have not simulated such systems,

however, it is possible to extend our methodologies to study crystallization from

solutions. In fact, we expect this to be more feasible when simulating such

processes due to the shorter times scales for molecular ordering.

(433:[433]433) Rasmita Raval remarked: Your paper is really interesting. A

major comment that can be made is that the roughness of the surface determines

the physical state of the adsorbed layer, i.e. you have shown that surfaces are

hydrophobic, hydrophilic, molecule-phobic, molecule-philic depending on their

roughness. This leads to the question, is there sufficient knowledge at present to

tune the state of the surface layer required simply by engineering surfaces

accordingly?

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Ahmad Jabbarzadeh responded: Thank you for your comments. I believe there

are methodologies that allow for the control of surface roughness at various

length scales using surface engineering methods.

(435:[435]435) Claire-Marie Pradier asked: Your model predicts that the

contact angle varies linearly with the lattice parameter; are you talking about the

periodicity of the pillar or the lattice parameter of the substrate surface?

Ahmad Jabbarzadeh replied: This refers to the dependence of wettability on

the lattice size of the smooth surfaces only, as shown in Figure 4 of our manuscript

(DOI:10.1039/C7FD00071E). We do not claim the dependence is linear,

however the trend line shown in this gure shows that the contact angle increases

with an increase in the lattice parameter. The gure should be considered as per

the conditions described in section 3.1.1.

(436:[436]436) Claire-Marie Pradier continued: Do you have experimental

evidence of this linear variation of the contact angle with the lattice parameter?

Ahmad Jabbarzadeh responded: The trend observed here is in general agreement

with the experimental evidence in ref. 1 that suggest that in single

component metallic melt-surface systems where weak van der Waals forces are

dominant, surface facets with higher atomic density will lead to better wettability.

Furthermore, experiments described in ref. 2 on metal–carbon interfaces have

shown that the contact angle of liquid metal on more compact facets of diamond

are smaller, demonstrating increasing atomic density (decreasing nearest

neighbour) results with decreasing contact angle.

1 P. Shen, H. Fujii and K. Nogi, Effect of substrate crystallographic orientation on wettability

and adhesion in several representative systems, J. Mater. Process. Technol., 2004, 155, 1256–

1260.

2 O. Dezellus and N. Eustathopoulos, The role of van der Waals interactions on wetting and

adhesion in metal/carbon systems, Scr. Mater., 1999, 40, 1283–1288.

(437:[437]437) Johannes Seibel asked: Did you also increase the surface

roughness to the point where there is no difference between the crystallization on

the nano-patterned surface and the crystallization on the smooth surface?

Ahmad Jabbarzadeh answered: No, but as can be seen from gures 14a and

14b in our paper (DOI: 10.1039/C7FD00071E), within the limits of roughly w¼\_5-

6 nm, or roughness ratio /1 the effect will vanish.

(439:[439]439) Angelika K¨uhnle opened a general discussion of the paper by

Markus Lackinger: Markus, I really enjoyed your detailed description of the moir´e

pattern. I wonder, though, why these slight rotations are observed. You can

envision that the energy landscape is very at. However, the layers are large and

a small energy penalty would add up to a large number. Wouldn’t it?

Markus Lackinger responded: Thank you very much Angelika. In principle, I

would agree, however, this argument implicitly assumes that the experimentally

observed TMA structures represent the energetically most favorable epitaxial

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relation to the graphite substrate. I believe that optimizing the adsorption

conguration of a single TMA molecule could result in a slight energetic advantage.

However, the network of strong hydrogen bonds in the quite rigid chickenwire

structure imposes constraints and dictates the mutual arrangement of

further TMA molecules. Hence, it appears unlikely that the other TMA molecules

can simultaneously optimize their interactions with the surface. Accordingly, the

corrugation of the surface potential averages out, even more so for increasing

domain size.

In fact, the emergence of moir´e patterns could be interpreted as an indication

of relatively weak molecule–surface interactions as compared to molecule–

molecule interactions. This argument even gains strength for incommensurate

structures, as proposed for the TMA chickenwire structure on graphite.

I would like to put an alternative explanation forward: the orientation of the

TMA domains is already determined at an early stage of growth, i.e. during the

nucleation. We propose that the critical nucleus has an energetic preference for

the observed 5\_ orientation. However, the potential well around this energetically

ideal orientation is rather shallow, and thermal uctuations facilitate small

deviations from the optimal orientation. Subsequent growth kinetically stabilizes

this domain orientation close but not necessarily equal to the ideal angle.

To test this hypothesis, I propose to grow TMA monolayers at low temperatures

in order to suppress the thermal uctuations. This can only be done in a UHV

experiment, where LEED would facilitate a direct and global measurement of the

respective orientation, or distribution of orientations, between TMA and graphite.

(441:[441]441) Steven De Feyter queried: Do you expect that the precision with

which you determined distances based on the appearance of moir´e patterns can

help to investigate other phenomena? For instance, would it be possible to probe

the impact of the thermal expansion of the graphite substrate on the structure of

the isophthalic acid monolayer? Could you use it to probe local stress caused by

host–guest chemistry (isophthalic acid–coronene)?

Markus Lackinger replied: Studying thermal expansion of the TMA network

would denitely make an interesting case. For one data point we have already

carried out the imaging at 50 ’\_C, but we did not nd any signicant deviations of

the lattice parameter. At the liquid–solid interface, the accessible temperature

range is rather limited at the lower end by freezing of the solvent. For elevated

temperatures, we have observed a discoloration of the solution, pointing towards

chemical reactions between solute and/or solvent molecules. This sets the upper

limit for the temperature. However, carrying out experiments in UHV would allow

us to study a wider range of temperatures.

A further idea would be to study static isotope effects with a deuterated version

of TMA. It is known that this affects the hydrogen bond length. However, the

effect is quite small, probably even below the accuracy of our method.

We have done some experiments with coronene guest molecules. If we add the

coronene molecules aer formation of the TMA network, we believe it just lls the

pores without causing a rearrangement of the TMA network. Thereby, the intramolecular

contrast of the coronene guest molecules becomes likewise modulated,

and the guests even enhance and amplify the moir´e pattern as previously

observed1, but the moir´e patterns are effectively similar to the pure TMA network.

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Yet, we found differences when the network is formed in the presence of coronene

molecules, resulting in small domains. This clearly shows an inuence of the

coronene guests on the TMA network formation process, however, we did not

observe moir´e patterns with a dened periodicity for these small domains.

1 S. J. H. Griessl, M. Lackinger, F. Jamitzky, T Markert, M. Hietschold and W. M. Heck,

Langmuir, 2004, 20, 9403–9407.

(442:[442]442) Vladimir Korolkov commented: Oen people look at the moir´e

patterns, some people look at them in great detail and some people just report

them, you observed quite a few moir´e patterns. However, in dry lms we have

observed only one pattern and never seen any other moir´e patterns. You quite

clearly see variations in moir´e patterns, is this possibly due to the presence of

a solvent layer and possible diffusion of the molecules within it? And a further

comment; the reality is with AFM, corrugation of the moire pattern, depending on

the molecular system, could be as small as a few picometres. So it is limited by

base noise levels in AFM and could be missed.

Markus Lackinger responded: This is a very interesting, and for me quite

surprising, result. I would indeed anticipate a distinct inuence of the different

preparation conditions. The occurrence of one unique moir´e pattern is a necessary

condition for thermodynamic equilibrium. However, nding equilibrium

structures in dried samples as opposed to the liquid–solid interface is counterintuitive

for me. I would have expected that equilibrium structures are more likely

to be observed at liquid–solid interfaces due to possibilities of dynamic exchange

between molecules in solution and on surfaces. So it would be denitely worthwhile

to look more into the details of your preparation protocol, i.e. the type of

solvent, concentration, method and speed of drying.

(444:[444]444) Peter Beton asked: Could small changes in the lattice constant

be an alternative explanation of the variation in angle and period of the moir´e

patterns? The energy variation for small changes in lattice constant appear very

small.

Markus Lackinger answered: In principle yes, yet the experimental observation

of a unique relative rotation between TMA and the graphite lattice of approximately

5\_ with only small deviations implies that the reciprocal lattice vectors of

the moir´e always occurs between the (7,1) TMA and the (1,0) graphite reciprocal

lattice points. In this respect, the theoretical curve of the moir´e orientation (with

respect to the TMA lattice) vs. the moir´e period in Fig. 6 of the manuscript (DOI:

10.1039/C7FD00113D) with the precise TMA lattice parameter as an additional

parameter can be considered exact. So for each moir´e pattern one data point can

be plotted which allows us to deduce a unique and exact value of the TMA lattice

parameter. Interestingly, all experimentally observed moir´e patterns result in

a similar TMA lattice parameter of 1.652 nm \_ 0.002 nm, suggesting that the main

reason for the different moir´e patterns is indeed small variations in the relative

rotational orientation between TMA and the graphite lattice. However, small

variations in the TMA lattice parameter within the experimental uncertainty of \_

0.002 nm cannot be excluded.

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Fig. 2 of the manuscript (DOI: 10.1039/C7FD00113D) provides additional and

more direct evidence for this hypothesis: the two TMA domains in the lower half

show a very small, but safely detectable relative rotation of \_1\_ and different

moir´e patterns. This very justied question could, and should, be experimentally

settled by precisely measuring the TMA lattice parameter either by LEED or

powder X-ray diffraction.

(446:[446]446) Jonathan Davidson said: There has been some discussion of

using LEED to further study these systems, but have you considered using powder

X-ray diffraction? This technique can achieve even higher levels of precision and

is ideally suited to the study of monolayers on HOPG substrates.

Markus Lackinger responded: I was not aware that monolayer sensitivity can

be accomplished with powder X-ray diffraction. I fully agree that the higher levels

of precision in the lattice parameter could be particularly useful for further

studies of TMA monolayers on graphite. Thank you very much for pointing this

out to me, we will denitely look into this type of experiment for further studies,

e.g. of the thermal expansion coefficient or isotope effects.

(447:[447]447) Deepak Dwivedi said: Thanks for the nice presentation. Can this

model be applicable to X-ray diffraction? As for reciprocal space lattice calculations,

we follow the Ewald sphere calculation which allows us to predict the

possible diffraction that could occur for the system. Can I apply your model to

monolayers or polycrystalline lms? I encounter monolayer or multilayer lms on

steel surfaces and am trying to explore the possibility of applying your model to

my system. If you could comment on this, it would be helpful.

Markus Lackinger responded: Emergence of these very dened moir´e patterns

of highly ordered molecular monolayers is presumably only observable on very

dened surfaces prepared according to surface science standards, i.e. atomically

at and clean. Hence, I would doubt that this will work on more technological and

presumably rough steel surfaces. I’m not sure if I understand the point about Xray

diffraction correctly. The main idea here is to use real space microscopy (i.e.

STM) images to acquire information about the moir´e pattern directly. Since the

moir´e pattern arises from the superposition of the surface and monolayer lattice,

additional information about the monolayer lattice parameters can be obtained

from the (generally known) surface lattice parameters.

(448:[448]448) Deepak Dwivedi asked: When we measure the lattice parameter

with X-ray diffraction, it involves various errors as diffraction depends on atomic

scattering, structure factors, thermal factors etc.. If you measure the lattice

parameter with those, it may involve some error. What would you recommend to

mitigate this issue? In your model you have taken a lattice parameter, was it

a modied one and free from these errors? How do you see your model applied to

solve this problem? Can we use this model to answer this question either directly

or indirectly?

Markus Lackinger answered: First of all I would like to state that using real

space measurements of moir´e patterns for the precise determination of lattice

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parameters for one of the two involved lattices is by no means a general method

and remains limited to special model systems, where TMA monolayers on

graphite appear particularly suitable. The input data, i.e. moir´e period and

orientation with respect to either graphite or the TMA lattice, are obtained from

high resolution STM images. So the accuracy of the method depends on the

accuracy with which these geometric parameters can be measured in real space

images. For geometric measurements in STM images, the limiting factors are

thermal dri, piezo hysteresis and piezo creep. Even though the proposed method

features relatively high precision as compared to directly measuring lattice

parameters from STM images, the high precision of an appropriately carried out

diffraction experiment cannot be attained.

(449:[449]449) Deepak Dwivedi continued: Out of curiosity, I wanted to ask

about the application of this model for predicting the effects of doping or

substitutional diffusion (either in single crystal monolayers or polycrystalline

multilayer lms), as we know that a change in the lattice parameter (Vegard’s law)

can suggest doping (insertion of some elements inside your unit cell changes the

lattice parameters). Do you think your model could be applied in this way?

Markus Lackinger responded: Vegard’s law proposes a linear relation between

the lattice parameter and composition for alloys, i.e. completely miscible systems.

Since we are looking at pure TMA monolayers on (also chemically pure) graphite

surfaces, I do not understand what is possibly meant by doping or substitutional

diffusion in this context. So I do not see a feasible way in which the model could

be applied for this.

(450:[450]450) Talat Rahman remarked: Whenever you have these moir´e

patterns arising from slightly incommensurate structures, a vibrational mode

should exist, a very low frequency mode, connected to the slushing of one

structure over the other. It is the so-called Goldstone mode. It should be possible

to measure it, and it gives you an idea about the strength of the interaction. Have

you thought about that? Another question, Would you see the kind of effect you’re

seeing here (multiple moire patterns) on any other substrate?

Markus Lackinger answered: As far as I know, vibrational spectroscopy data for

TMA monolayers on graphite are not available. Admittedly, I have not thought

about the Goldstone mode so far, but this is denitely an interesting suggestion

and it is worthwhile to look deeper into the details. These moir´e patterns are

easily observed by STM in particular, thus limiting the choice of possible alternative

substrates to electrical conductors. In general, the molecule–surface

interactions are stronger on metals. This fact bears two implications: (1)

commensurate structures with dened equivalent adsorption sites become

increasingly more likely, and (2) on even more reactive surfaces, such as Cu(111),

deprotonation of the carboxylic acid groups and subsequent formation of metalcoordination

bonds with surface adatoms inhibits self-assembly of the hydrogen

bond network. With Au(111), on the other hand, the chickenwire structure was

observed, yet with an additional contrast modulation through the herringbone

reconstruction. So one could think of other weakly interacting surfaces, such as

MoS2 or appropriately passivated metal surfaces.

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(451:[451]451) Rasmita Raval asked: Do you think entropic effects and the

inherent anharmonicity of hydrogen bonds are important in stabilizing your

incommensurate structures?

Markus Lackinger answered: Your question already implies that the observed

structures are the thermodynamically most stable structures. However, the

observation of different moir´e patterns indicates that the observed TMA structures

have slightly different epitaxial relations to graphite.

Even though we cannot rigorously prove it, we propose that the precise nal

orientations of the TMA domains are already determined in the nucleation phase,

where only an approximate orientation with respect to graphite is preferred, but

small deviations are still possible. The absence of domain ripening also suggest

that the orientation of larger domains is xed by kinetic entrapment.

Models suggest that the occurrence of incommensurate superstructures is

a question of the relative strength of adsorbate–adsorbate vs. adsorbate–substrate

interactions, where signicant insights can already be obtained from relatively

simple 1D models.1 These conditions appear to be met by TMA monolayers on

graphite, where the two-fold cyclic hydrogen bond between TMA molecules is

relative strong, whereas DFT calculations suggest a relatively small corrugation of

the surface potential. So for this type of explanation the anharmonicity is not

necessarily needed, but of course more subtle effects cannot be ruled out.

1 P. Bak, Rep. Prog. Phys., 1982, 45, 587.

(452:[452]452) Claire-Marie Pradier queried: You never observed an inuence

of the solvent, is this not surprising?

Markus Lackinger response: For TMA, solvent-induced polymorphism is well

documented, resulting in the so called ower-structure for shorter chain length

fatty acids as solvents.1 So we have deliberately chosen two solvents (heptanoic

acid and nonanoic acid) for our studies that both afford the same chickenwire

structure. For these two solvents, we nd a similar orientation of the TMA lattice

with respect to the graphite lattice, resulting in comparable moir´e patterns and in

experimentally indistinguishable TMA lattice parameters. This may be taken as

indication that the specic solvent does not affect nucleation and growth of the

TMA chickenwire polymorph, and does not affect the intermolecular hydrogen

bond strength and length, e.g. by screening effects that should depend on the

dielectric constant of the solvent.

Overall, this can be taken as evidence that the molecule–molecule interaction

in the TMA chickenwire structure is by far dominating over any other possible

inuence.

1 M. Lackinger et al., Langmuir, 2005, 21, 4984–4988.

(453:[453]453) Steven De Feyter commented: What is the origin of the

appearance of moir´e patterns in the STM images? Is it an electronic effect or is it

the result of slight topographical changes in the monolayer?

Markus Lackinger replied: In principle both are possible, but I’m inclined to

believe that electronic effects dominate. Oand, I could not imagine any

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strongly site-specic TMA–surface interactions that would possibly cause the

tilting of TMA molecules and hence buckling of the monolayer, even though

simulations propose that the oxygen atoms of the carboxylic acid groups might

interact more strongly with the graphite surface.1 On the other hand, we also have

tried to study the moir´e corrugation as a function of tunneling voltage. However,

in contrast to what would be expected for an electronic origin, we could not nd

any systematic dependency. Maybe complementary NC-AFM experiments that are

more, but not exclusively, sensitive to topographic effects could shed more light

on the origin of the moir´e patterns. Appropriate calculations would also have the

potential to address this question, however, these would have to deal with the

incommensurability of the TMA monolayer on graphite.

1 F. Shayeganfar and A. Rochefort, Langmuir, 2014, 30, 9707–9716.

(454:[454]454) Angelika K¨uhnle said: I want to comment on the issue of

whether or not one can differentiate topography and/or electronic effects as an

origin of the moir´e patterns using AFM. It was kind of suggested that you can use

AFM to measure topography. However, like any other SPM technique, AFM does

not reveal a signal that exclusively originates from topography. In fact, AFM

measures forces. Of course, by combining information from STM and AFM, one

gains complementary information, which is oen helpful.

(500:[500]500) Ioan Bˆaldea opened a general discussion of the paper by James

Batteas: I amconfused. In your experiments, you see that the I–V curves measured

on the one day clusters are qualitatively different from the I–V curves recorded

over the three day and ve day clusters. However, the argumentation put forward

in your paper on why the one day clusters behave differently from the three and

ve day clusters has nothing to do with that of your ve minute presentation.

In your paper, you based your argument against charge transport via tunneling

in the three and ve day samples on the impossibility of tting the measured I–V

curves with cubic polynomials. In two recent papers,1–2 I discussed in detail the

shortcomings of cubic polynomial approaches and the fact that they are unable to

correctly describe charge transport via tunneling, therefore I will not refer to this

issue here.

In your ve minute presentation you claimed that, in contrast to the one day

samples wherein charge transport proceeds via tunneling, in your three and ve

day samples the charge transport proceeds via hopping, and you referred to

a Coulomb blockade, a notion that cannot be found in your paper. I would note

that strong I–V nonlinearities like those you have measured (cf. your Fig. 4, DOI:

10.1039/C7FD00118E) are quite unusual for a hopping mechanism; typical I–V

curves do not so strongly depart from linearity. As a constructive suggestion (the

above remarks are not intended as polemics), in order to get more insight into the

conduction mechanism you may consider performing transport measurements at

variable temperatures and see, for example, whether the transport is thermally

activated or not.

1 I. Bˆaldea, Phys. Chem. Chem. Phys. 2015, 17, 20217.

2 I. Bˆaldea, Phys. Chem. Chem. Phys. 2015, 17, 31260.

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James Batteas replied: Thank you for your comments. With regards to the

criticism about the charge transport for 3 and 5 days. The truth is that we are fully

clear on how to describe the charge transport for the aged clusters. This is

a common problem with all molecular electronics, and other groups (e.g.

Whitesides, McCreery) have also observed such phenomena that they cannot

explain (e.g. transport over huge distances, >30 °A, without temperature dependence).

It is true that describing this as hopping or Coulomb blockade may be

more confusing than helping. But we have certainly seen this in our prior low

temperature (\_4 K) measurements on such clusters made in cross-wire junctions,

and expect a similar effect here.1

The differences between “hopping” and “tunneling” are much smaller than

normally assumed (there is an excellent review by X.Y Zhu2). It mostly refers to the

residence time of the passing charge or its degree of occupation of a molecular

level (this is also explained in the papers by Galperin, Ratner and Nitzan noted in

our paper - see reference 16, DOI: 10.1039/C7FD00118E). As the molecular level

gets closer in energy to the Fermi-level the transport gains more “hopping character”.

The important effect of the aggregation is to change the energy of the

molecular levels, either by narrowing the HOMO–LUMO gap or by stabilizing the

excited state (i.e. it is easier to charge the molecule within a hopping view).

It is also correct that for the 3 and 5 day clusters it is possible that the charge

propagates through the molecule via tunneling. In this view, the 3 and 5 day

clusters would have many energy levels within the \_2 eV that we measure, and

these would produce the sharp steps in conductance (or resonances). What we are

really suggesting is that a new conduction channel is opened, which can be

understood as either near-Fermi DOS or a completely different effect, like

charging of the molecule.

With regards to the tting, while we recognize the challenges with the cubic

model, here we have only used the tting to the cubic model in a qualitative

manner. The argument that the one day clusters can be tted to a single tunneling

channel while the 3 and 5 day clusters cannot, holds regardless of the choice of

model (cubic, single model, Simmons, super-exchange – those tunneling models

which are simplistic enough to have an analytical form), and perhaps a better

distinction is between “off-resonance-tunneling” for the one day and either

“resonance tunneling” or “hopping” for the aged clusters.

In summary, our analysis is not perfect and we continue to seek better solutions.

We are also actively seeking to carry-out additional low temperature STM

measurements to continue to evaluate on a cluster-by-cluster basis the thermal

effects, but rst we are trying to create well dened cluster structures whereby the

local organization can be well controlled, since this will be the only way to then

denitively address these questions

1 A. E. Schuckman et al., J. Phys. Chem. C., 2015, 119, 13569–13579.

2 X.-Y Zhu, J. Phys. Chem. B., 2004, 108, 8788–8793.

(501:[501]501) Ioan Bˆaldea remarked: I think that extra characterization of

your samples would be highly desirable in order to get more insight into the

differences between the one day clusters and the three and ve day clusters. It

would be useful if you can measure frequency-dependent transport, possibly

supplemented by measurements of vibrational properties, which may provide

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information on the adsorption of your porphyrin-based clusters on the Au(111)

substrate.

James Batteas replied: This is an excellent suggestion and we are very keen to

carry-out AC tunneling spectroscopy on these. In our previous work, we have

examined the low temperature inelastic tunneling spectra of similar porphyrin

islands, and that is described in detail in the paper noted here.1

1 A. E. Schuckman et al., J. Phys. Chem. C., 2015, 119, 13569–13579.

(502:[502]502) Manfred Buck said: Referring to the Coulomb barrier observed

for the porphyrin thiols, you mentioned the contribution of molecular levels and

aggregation. Could you explain their contribution in more detail. Is this effect

dependent on the type of porphyrin, e.g. whether the porphyrin is metallated or

not?

James Batteas answered: The systems we have seen where this occurs have only

thus far been in the metallated porphyrins. We have seen this here with the Zn triphenyl

porphyrin thiol version as well as in our earlier studies of tri-pyridyl

porphyrin thiols with Zn.1 Our hypothesis for this is that the charging energies

of the individual molecules are too large, but are reduced to a suitable level (i.e.

<0.2 eV) when an aggregate of >5–10 nm in lateral dimension is formed via pistacking.

1 A. E. Schuckman et al., J. Phys. Chem. C., 2015, 119, 13569–13579.

(503:[503]503) Steven De Feyter asked: To what extent are the time-dependent

effects, i.e. the changes in the monolayer structure, affecting any "practical"

applications and how do you deal with them?

James Batteas responded: This is actually a very important point. The timedependent

uctuations in the structures will presumably impact their local

order and in that regard also their local electronic properties. Only in having wellde

ned and ordered structures with minimal variations would you one be able to

predictably control the transport if the focus was, say, specically electronic

switching for molecular electronics. For systems such as dye sensitized solar cells

however, I would expect reduced sensitivity to these local effects so long as the

cluster size was sufficiently large.

(504:[504]504) Claire-Marie Pradier remarked: Surprisingly, when the time of

immersion increases, the thiols tend to desorb and the porphyrin islands shrink;

can you comment on that?

James Batteas replied: We believe that the change in cluster size is from a reorganization

of the porphyrins in the islands to adopt a more pi-stacked (more

closely packed) conguration. The loss of thiols that is observed is due to the

desorption of the surrounding dodecanethiol matrix back into solution. This has

been seen routinely for alkanethiols on Au when the samples are soaked in

solvents such as dichloromethane or ethanol.

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(505:[505]505) Han Zuilhof asked: Firstly, have you considered using multisulfur

moieties (such as tri-S-adamantane-like systems or even simple di-thiol

systems) which can couple your tetra-phenyl system to stabilize interactions

with the surface? Secondly, regarding the tetra-phenyl system, why did you pick

that in the rst place, rather than a para-di-phenyl system in which the in-plane

steric hindrance (with either the alkyl monolayer or adjacent porphyrin system)

would be much (somewhat?) smaller?

James Batteas responded: Yes we have, and in fact we have molecular systems

with two alkylthiol linkers to the surface, but we have yet to explore them in detail.

We picked this system (actually originally a tetra-pyridyl system) with the vision in

mind of building larger hierarchical 3D structures through additional metal–

ligand binding. This phenyl ring system was chosen to simply follow along the

same lines, but to eliminate possible metal–ligand binding between neighboring

molecules. Certainly a para-di-phenyl system (as you suggest) would also be

a reasonable choice.

(506:[506]506) David Amabilino commented: Regarding the last point, the

tripyridyl system you talked about. There’s a system out there, I’m sure you’re

aware of, where they grow a ferrocene dendrimer off the surface.1 Could you say

what you think about that system with respect to yours, given the results you’ve

seen, especially thinking about the stability of alkyl or aromatic thiolate monolayers

on gold?

1 R. Sakamoto, S. Katagiri, H. Maeda, Y. Nishimori, S. Miyashita and H. Nishihara, J. Am.

Chem. Soc., 2015, 137, 734.

James Batteas responded: The system they have shown is very interesting.

Stable redox centers, such as Fe, in their paper provide a nice route toward

directing hopping in molecular systems. We have considered creating similar

assemblies with our pyridyl system to create hierarchical structures that could

direct energy ow via vectoral energy transfer, but it is clear from their work, that

directing electron ow would also be possible. With regards to your comment on

alkyl vs. aromatic thiol subunits, the stability of both attachment groups is

similar, and both suffer long term oxidation effects to sulfonates, which limits

their applications in some devices.

(507:[507]507) David Amabilino said: I was a little surprised from looking at

Fig. 1 in your article (DOI:10.1039/C7FD00118E), which shows different sized

clusters. Why is it that the large ones you see just aer immersion have

a completely different behaviour to the ones where you have a long immersion

time and then you start to get bigger clusters? How is it different to the initial

immersion stages?

James Batteas responded: Our proposed model is that the large aggregates

formed in the initial immersion stages are more disordered than those seen

following longer immersion times. Here, we suggest that the initially disordered

islands slowly organize into more closely pi-stacked structures that are then also

more electronically coupled, allowing them to act almost like an "organic

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quantum dot”. This local reorganization is suggested based on the observed

reduction in island size as a function of time as the porphyrins in the islands form

more closely pi-stacked structures. This results in the reduced charging energies,

and contributes to a small HOMO–LUMO gap.

(508:[508]508) Amar Flood commented: Regarding the parameters that you

have available to dial in the polaron stability, you spoke about extending the size,

and increasing pi-stacking. Are there other extraneous experimental parameters

you might be able to introduce, e.g. solvent vapors, to stabilize the build-up of

charge that constitutes a polaron? What features of the system (chemical or

physical attributes) could support a polaron besides pi-stacking?

James Batteas responded: That is an exceptionally interesting suggestion!

Carrying out these studies in a solvent that could further help stabilize the charge

on the islands would be quite interesting. Here, we could explore how something

like phenyloctane vs. octanol would impact this.

(511:[511]511) Rasmita Raval said: It would appear that a critical number of

your functional porphyrin-thiol units have to self-assemble locally in order to

create the requisite function. Do you know what “magic” combination is required

for a working unit? Presumably the surrounding sea of C12 molecules is critical in

achieving this, can you comment on this please?

James Batteas replied: What our proposed model suggests is that for the

voltage range we are measuring (\_ 2 V), the island dimensions must be on the

order of 5–10 nm in order for the charging energy to be sufficiently reduced to

observe controlled switching. It is our intention to carry forward a number of

patterning experiments to design well organized clusters of specic dimensions

to create a clear correlation between the specic sizes, local molecular organization

(i.e. degree of order) and the observed electronic properties.

Here we are also seeking to address the instabilities of the surrounding C12

molecules. Since we have seen their desorption and transition to lower density

structures for the longer assembly times, we are now planning to replace them

with diacetylene containing thiols of the same chain length where we can photocrosslink

the matrix molecules to increase their stability and hopefully further

stabilize the resulting porphyrin-thiol clusters.

(512:[512]512) Peter Beton asked: Looking at your models of the cluster, is

there a possibility of (or have you already been) looking at the optical properties?

Porphyrin clusters should change their uorescence peak positions, are any shis

observed?

James Batteas responded: We have attempted to look at the optical spectra on

the surface, but the very low densities have been prohibitive in obtaining sufficient

signals (of either absorbance or uorescence) for us to evaluate the expected

changes in optical spectra that would accompany aggregation. To do this, we

would likely need to carry-out near-eld spectroscopy measurements, which we

currently do not have the capabilities to do.

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(513:[513]513) Peter Beton continued: You give a gure in your paper of about

6 nm for the pi-pi stack, that seems a bit bigger than the gure that’s normally

quoted?

James Batteas responded: Yes, this is a bit larger than normally reported. We

have found in our prior STM studies a pi-stacking spacing of 0.5–0.6 nm,1 which is

slightly larger than the value of 0.3 nm seen for many other pi-pi systems. We

attribute this larger spacing to the steric hindrance associated with the canted

phenyl rings on the porphyrin macrocycle. We have also carried out DFT calculations

for dimers of these types of molecules and nd a similar 0.5–0.6 nm

spacing for the energy optimized structure.

1 A. E. Schuckman et al., J. Phys. Chem. C., 2015, 119, 13569–13579.

(514:[514]514) Rasmita Raval opened the discussion of the paper by Julien

Gautrot: Really nice work. How much is understood about the nano-protein layer

that is formed, which appears to be the key to how the cell subsequently reacts

and behaves?

Julien Gautrot responded: Very little is known of the structure and properties

of such protein layers. In the case of the interfaces generated between the uorinated

oil studied and the culture medium used for HaCaT cells, we characterised

the mechanical properties of the interfaces generated and found

differences in interfacial shear properties. Further studies will characterise the

interfaces generated as well as other designs fully.

(516:[516]516) Claire-Marie Pradier commented: You describe the role of

protein adsorption on cell adhesion; can it be considered similar to the

mechanics of biolm formation known to start with proteins and extracellular

polymer adsorption?

Julien Gautrot replied: There are similarities in the fact that proteins and other

biopolymers are assembled at interfaces by bacteria to help stabilise biolms.

Differences are in the importance of the local, nanoscale, mechanical environment

of the adsorbed layers. Biolms do not exert contractile forces, but the

extracellular matrix may help biolms resist macroscopic mechanical challenges.

(517:[517]517) Yuri Diaz Fernandez asked: Regarding the rheology data in

Fig. 5 of the paper (DOI: 10.1039/C7FD00091J), if I interpret this correctly, the

protein lm is formed irrespectively of the presence of the surfactant. Could you

comment on the function of the surfactant on the proliferation of the cells on the

interface?

Julien Gautrot responded: This is correct. In this respect, PFBC is perhaps

better described as a co-surfactant and proteins contained in the tissue culture

medium are thought to act as the primary surfactant. What we propose is that the

co-surfactant is strengthening the mechanics of the protein lm formed at the

interface.

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(520:[520]520) Claire-Marie Pradier remarked: There’s an ongoing controversy

about the scale (size of the surface defect or roughness), which can inuence cell

adhesion. It is even claimed that defects on the nanoscale may inuence cell

adhesion. Could this be related to, e.g., protein adsorption?

Julien Gautrot responded: Integrins are important surface receptors mediating

cellular sensing of the extra-cellular matrix. Spacing between such integrins in the

range of 60-70 nm has been proposed as a critical distance to sustain the

formation of focal adhesion and the establishment of a stable cytoskeleton (see

the work of Spatz). That was proposed to correspond to the distance between

integrins in clusters preceding the formation of focal adhesions, and the distance

between ligand sites on ECM bres such as collagen bres. Hence, a direct

sensing of ligand assembly at scales below this critical distance would require

other mechanisms rather than simple geometrical considerations. For example,

nanoscale changes in surface chemistry (roughness, slight changes in the

chemical composition of the surface such as in monolayers or in polymers or

ceramics with very slight differences in chemistry) can have an important impact

on the adsorption of proteins and the structure/morphology of the assemblies

formed (see the work of Salmeron-Sanchez). This in turn may signicantly impact

cell phenotype, so indirect effects. That being said, integrins have been shown to

be sensitive to synergistic ligand binding (RGD/PHSRN for example), with spacing

below this critical distance.

(521:[521]521) Claire-Marie Pradier asked: In your paper, you mention a PDMS

material surface whose exact composition was not given, do you have any ideas

about this? And could it inuence protein adsorption?

Julien Gautrot replied: That is correct, we do not know the precise composition

of the interface formed between Sylgard 184 (a silicone material routinely used in

microfabrication). It is reasonable to expect albumin molecules to adsorb at the

surface of liquid silicone as they do to many other hydrophobic surfaces and

liquids, but the molecule(s) that may be involved in the further maturation of the

associated interfaces (from a physico-chemical and mechanical point of view) are

not known. Vinyl functions present in Sylgard 184 would not be expected to

directly result in protein conjugation under the experimental conditions used, but

they are abundant in Sylgard 184. Other molecules that may be present are

residual monomers from the synthesis of the silicone polymers.

(522:[522]522) Ahmad Jabbarzadeh asked: Have you measured, or do you have

an estimate of the thickness of the protein interface between PDMS and the cell?

Do you expect the results to be dependent on the thickness?

Julien Gautrot replied: We have measurements of thicknesses in the case of

other systems, but not the particular case of interfaces conditioned with medium

or serum. Typically, thicknesses measured for protein adsorption at the surface of

hydrophobic oils are in the range of 30 to 50 nm.

(523:[523]523) Stuart Clarke opened a general discussion of the paper by Han

Zuilhof: It’s nice to see other techniques being developed in this area. As

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mentioned previously, there are a suite that can now be used for these complex

solid/liquid interfaces, each providing part of the story. In this case, I might

suggest neutron reectivity for consideration.

The neutron reection method is in situ (the adsorbed layers remain in the

liquid and can be studied without removal or drying) and the approach is nondestructive.

One can determine the absolute composition (mol m:2) and some structural

information, particularly the structure normal to the surface (oen represented as

layers). However, usually there is limited in-plane structural information and

other approaches are preferred.

Although not an inherently fast method, due to the relatively low ux of

neutrons, in favourable cases timescales of second/minutes should be accessible,

which should be suitable for the particular problem of interest here. There are

some much faster neutron reection methods (such as stroboscopic approaches)

which can assess much faster changes.

Importantly, isotopic variation enables one to highlight the behaviour and

location of different components in a complex system (particularly hydrogen vs

deuterium). In this case, for example, the binding of the hydrogen bonded guest

should be readily accessible.

See the studies of Bob Thomas and Jeff Penfold.1-2

Question: We have a little experience with MS and have struggled to get

quantitative data (in absolute units). Partly this arises due the competition of the

different components for ionisation. Hence, the same amount of a component of

interest, in the presence of different amounts of other species, can give different

ion intensities at a xed m/z. Hence, although we can readily follow changes in

a component, the concentration is not generally absolute. Do you have any helpful

comments on this matter?

1 G. Fragneto, R. K. Thomas, A. R. Rennie and J. Penfold, Neutron Reection from Hexadecyltrimethylammonium

Bromide Adsorbed on Smooth and Rough Silicon Surfaces,

Langmuir, 1996, 12, 6036–6043

2 A. R. Rennie, E. M. Lee, E. A. Simister and R. K. Thomas, Structure of a Cationic Surfactant

Layer at the Silica-Water Interface, Langmuir, 1990, 6, 1031–1034.

Han Zuilhof replied: In response to your comment, we have simply never

considered neutron scattering as a tool – it may indeed be interesting to study the

supramolecular binding of a well-studied case (for now: our UPy system) to

investigate the potential thereof. I will undertake further interactions with Dr

Clarke to see what might be feasible.

In response to your question, there are 2 facets to be considered here. First, the

intrinsic noise in a technique like DART-MS, that is intrinsic to it being an

atmospheric MS technique. The standard deviation can, in principle, be reduced

to <10% by repetitive measurements. This is the reason why all our MS

measurements are done in hexaplet. In addition, we look at the development of

an MS signal over time – this can be benchmarked in individual cases by, e.g.,

independent XPS measurements. However, if the question is: can we, from

a single measurement (even if performed in e.g. hexaplet), determine how much

material is on the surface? Then the answer is: no, since the ionizability of

compounds and issues like ion suppression might play a role. So we have highly

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accurate, but relative amounts. Great for kinetics, not (at least not via a trivial

method) for quantication on a surface. In the latter case, XPS is to be preferred.

(524:[524]524) Steven Tait commented: The system you studied here is covalently

linked to the surface with a quadruple hydrogen bond to the upper part of

the adsorbate. Is this type of conguration necessary for the DART method?

Would you please comment on what types of samples the DART method is able to

analyze? Can the charge state and other chemical characteristics of the sample be

analyzed accurately by DART?

Han Zuilhof responded: We analysed a great variety of monolayers in the past;

see some of our papers for examples.1–2 From these studies we learned which

groups cleave easily under these DART conditions, and which groups do not (or

do not yield recognizable fragments). The structure of the UPy dimer system was

chosen in such a manner that the most easily cleavable moiety would be the Hbonds.

In other studies, we have built-in an easily cleavable reporter moiety in

the groups, so as to be able to monitor the formation of even highly stable groups,

as in a Diels Alder reaction. See, e.g., ref. 3, especially Figure 3. Regarding

monitoring the charge state (e.g. of inorganic or hybrid complexes), I am afraid to

have to say I do not know, but think I amin the company of about 7 billion others.

Likely, the ionizability will be determined partially by the oxidation state, but I am

not aware of studies of this facet. This is certainly something of interest for

further work.

1 R. K. Manova et al., Ambient Mass Spectrometry of Covalently Bound Organic Monolayers,

Chem. Commun., 2013, 49, 922–924.

2 R. K. Manova et al., Ambient Surface Analysis of Organic Monolayers using Direct Analysis

in Real Time Orbitrap Mass Spectrometry, Anal. Chem., 2014, 86, 2403–2411.

3 R. Sen et al., Angew. Chem. Int. Ed., 2017, 56, 4130–4134.

(525:[525]525) Olga Barykina asked: Is there any restriction on the surface of

the analyzed material? Can it be an organic pigment surface or any other surface

made of small organic molecules? Is DART analysis suitable for this? How do you

subtract signals from the surface itself? Do you run the background?

Han Zuilhof responded: There are no restrictions. We analysed plastics,

inorganic materials – at and micro/nanostructured surfaces, etc. – DART is, as far

as we have seen, limited to the analysis of “relatively small” molecules, such as m/

z <2,000. Subtraction is not required, as the substrate typically does not display

these signals (namely, masses measured with a precision of 4 digits, e.g. 234.5678

amu. In addition, the m/z ratio should be > ca. 100, as otherwise the atmospheric

background is too high.

(526:[526]526) Giovanni Costantini said: Could you please comment on

differences or similarities between DART and DESI?

Han Zuilhof replied: Both DART and DESI have their own positives and

negatives in the study of surface-bound materials. Given their different modes of

ionization, each also yields slightly different fragmentation patterns.

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We have both types (DART and DESI) in our lab, and used both. In our hands,

DART turned out to be much more stable (it works all of the time...) than DESI,

and by now we have almost turned to DART exclusively.

There are again other, more recent, ionization sources that we are also using,

such as LAESI. This offers a clearly better lateral resolution than DART for

imaging MS, but requires sufficient water to ionize a sufficient amount of material.

Our organic monolayers on surfaces are not so suitable for that, but, for

example, coatings on bres that we recently studied with that technique worked

beautifully.

(527:[527]527) Karl-Heinz Ernst asked: I would also like you to compare DART

to different techniques like ToF-SIMS, for example. You could use these techniques,

freeze the sample, go into vacuum, and then you have depth proling

through thicker layers, or chemical imaging of cells that were cut in slices with

a microtome, then you have lateral resolution plus depth information. Do you

think you can install lateral resolution in your system by scanning the beam in X

and Y?

Han Zuilhof answered: Yes, lateral resolution is available (we have it routinely

on our system), and limited by the width of the DART beam. While this can be

optimized to the 100 micron scale (in the literature, not by us), ToF-SIMS allows

for a much higher lateral resolution: with DART this is typically on the scale of

hundreds of microns. However, DART is much milder, and really limited to the

top nanometers of a sample. In addition, DART-HRMS can be used on a Tuesday

for DART-HRMS measurements of a monolayer, be decoupled (in 5 min) to turn

into an LC-MS on Tuesday night and Wednesday, and be transformed (within 30

min) back into a DART-HRMS system again by Thursday morning. In other words,

the versatility of use is much bigger, and the costs very low (you probably already

have a suitable MS in your department, and a DART source costs only \_25k $).

(528:[528]528) Pol Besenius commented: I enjoyed your talk and paper, and I

think your analytical approach is very elegant for people that are interested in the

preparation of dynamic and functionalised surfaces. With respect to your

exchange kinetics of the UPy units, your schematic picture is a bit misleading

given that both the surface-bound and solution based quadruple hydrogen bond

units do self-associate into dimers. Have you looked into this using spectroscopic

tools and is the self-association important for the kinetics of the formation of the

heterodimers? In addition, would you expect the exchange kinetics to be faster if

you were to apply a hydrogen bonding partner in solution that has a much lower

driving force for the formation of self-complementary dimers?

Han Zuilhof replied: First of all: yes, the ChemDraw based cartoon simplies

the situation a lot (but is hopefully not misleading). As we demonstrate and

discuss extensively in the paper, there are eventually free (unreacted) NH2 groups,

undimerized UPy moeities, surface-bound UPy moieties dimerized with other

surface-bound moieties, and surface-bound UPy moieties dimerized with UPy

units coming from solution. The latter take up only about 10% of all surface sites.

The self-interaction of surface-bound UPy units is important. Perhaps the

clearest picture thereof comes from our modelling studies, which show extensive

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self-dimerization of surface-bound UPy units as long as no soluble UPy units are

around, and still signicant self-dimerization with the soluble UPy units present.

Your nal question is an intriguing one (as well as the suggestion for NaPy

derivates that you made). We are not fully sure of the answer, but/and think that

this is indeed a great topic for further studies.

(532:[532]532) Rasmita Raval remarked: I can see the value of your DARTHRMS

technique in identifying molecular species at an interface and indicating

the strength of their interaction at that interface. However, I am unclear about

whether it gives us mechanistic information on the specic nature of the selfassembly

or supramolecular chemistry that is involved. Can you please elaborate

on this? Would it be possible, using highly dened interfaces, to create

a database that would allow specic binding events to be recognised using DARTHRMS?

Han Zuilhof responded: The issue is what “specic nature” means here. As

shown in the paper, DART-HRMS has provided rate information for supramolecular

processes in a very facile manner. This is a big plus, as such rate information

for unlabelled systems is rare to absent up to now. In addition, by

measuring forward and backward rates, it allows us to derive equilibrium data.

That is also a big step forward for supramolecular processes at a surface.

Currently, I would argue that binding events that are in the range of k ¼ 102 : 108

M-1 should be measurable, if the components are in the mass range of DARTHRMS.

Such a range would, indeed, allow for the formation of a database, but

with the current range of processes truly studied in detail (only one, namely our

UPy case, with a few more in the pipeline), this needs to be shown in the coming 5

years.

(535:[535]535) Steven De Feyter asked: A question on sample preparation. To

what extent does sonication affect the results (at the level of dimerization)? Does

sonication have an impact on the nal structure?

Han Zuilhof answered: The results of sonication depend on the solvent. In

solvents like toluene, DCM, etc., we only nd removal of the physisorbed, nonspeci

cally attached material. In other words, aer the fast removal of some

fraction of UPy-based material, we observe a plateau intensity. We attribute this

plateau to only H-bonded UPy molecules. This plateau is fairly stable, as the

energy involved in sonication is not so large as to break up the H-bonded UPy

dimers. Prolonged sonication very slowly removes material from the surface, but

we did not study to which degree this loss of H-bonded dimers is aided by the

sonication (rather than just being an unassisted reverse process). In good solvents

the dimer is breaking up, and sonication speeds this up slightly.

(536:[536]536) Claire-Marie Pradier asked: To measure the amount of attached

UPy dimers, you calculate the F over P ratio, obtained by XPS, right? Did you

consider attenuation by the organic layer, plus the difference in the sensitivity

between F and P?

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Han Zuilhof responded: Yes, we measure F/P. Also, N/P is informative. We do

correct routinely for differences in the sensitivity using response factor corrections

– for the rst (taking account of the attenuation) we did not, given the

relatively thin layers (typically 1.5–2 nm) –for such scales the attenuation is

measurable, but not so big.

(537:[537]537) Claire-Marie Pradier opened a general discussion on the topics

raised during the session: Would anyone like to comment on the techniques one

should/could use to characterize surfaces under vacuum? I would like to mention

IR spectroscopy, applied in the reection mode, at grazing angle. It’s a very

sensitive technique which gives information about the nature of the chemical

groups that are present, even at the monolayer scale, in addition to XPS, as well as

on the molecule orientation/conformation.

Deepak Dwivedi responded: We have used Raman spectroscopy to characterize

the lm formed on carbon steel substrate and it was an in situ characterization,

but at the same time, I would like to mention that it was not under vacuum.

I think it is possible to make cells which can work under vacuum. Making cells

similar to in situ TEM cells can be helpful in this regard.

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