Surface-Bound Quadruple H–bonded Dimers: Formation and Exchange Kinetics

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Table of Contents:

1. Materials and Methods S2
2. Synthesis S3
3. NMR Data S7
4. Surface Preparation and Kinetics Determination S12
5. Supplementary Figures S17
6. Supplementary Tables S40
7. Material Studio Data S41
8. References S55
1. Material and Methods

Materials. Unless otherwise specified, all chemicals were used as received without further purification. 6-Methylisocytosine, 1,6-hexamethylene diisocyanate, 4-iodophenyl isocyanate, 4-(Trifluoromethyl)phenyl isocyanate, hydrochloric acid, methanol, hexane, acetone, dichloromethane, 2-propanol were purchased from Sigma-Aldrich. 12-Aminododecylphosphonic acid hydrochloride salt was purchased from SiKÉMIA. Aluminium pieces (99.5% purity, mirror polished, Staalmarkt Beuningen BV) were cut using mechanical cutter into exactly 2×1 cm or 1×1 cm dimensions. For surface modification reactions, the samples were loaded onto a specially constructed PTFE wafer holder able to hold up to 16 samples at a time thus ensuring rigorous reproducibility between samples.

Grazing Angle Total Reflection Fourier Transform Infrared Spectroscopy (GATR–FTIR). GATR–FTIR spectra were recorded with a Bruker Tensor 27 FT–IR spectrometer using a commercial variable-angle reflection unit (Auto Seagull, Harrick Scientific). A Harrick grid polarizer was installed in front of the detector and was used for measuring spectra with p-polarized radiation with respect to the plane of incidence at the sample surface. Single channel transmittance spectra were collected at an angle of 35° using a spectral resolution of 2 cm\(^{-1}\) and 2048 scans while flushing with dry N\(_2\). Obtained spectra were referenced with a freshly cleaned and etched aluminium sample.

X-ray Photoelectron Spectroscopy (XPS) Measurements. The XPS analysis of surfaces was performed using a JPS–9200 photoelectron spectrometer (JEOL, Japan). Survey and high-resolution spectra were obtained under UHV conditions using monochromatic Al K\(\alpha\) X-ray radiation at 12 kV and 20 mA and an analyzer pass energy of 50 eV for wide scans and 10 eV for narrow scans. The emitted electrons were collected at 10° from the surface normal (take-off angle relative to the surface normal 10°). All XPS spectra were evaluated by using
Casa XPS software (version 2.3.15). Survey spectra were corrected with linear background before fitting, whereas high-resolution spectra were corrected with linear background. Atomic area ratios were determined after a baseline correction and normalizing the peak area ratios by the corresponding atomic sensitivity factors (1.00 for C1s, 1.80 for N1s, 2.93 for O1s, 4.43 for F1s, 1.18 for P2s, 33.64 for I3d and 0.54 for Al2p).

**DART-HRMS Measurements.** Analysis of the modified aluminium surfaces was performed using a DART-SVP ion source (Ion-Sense, Saugus, MA) coupled to a Q-Exactive orbitrap high-resolution mass spectrometer (Thermo Fisher Scientific, San Jose, CA, USA), mounted on a motorized rail travelling at 0.2 mm/s. Thermo Scientific Xcalibur software (V2.1.0.1139) was used for data acquisition and processing. The measurements were performed in negative mode at 550°C using a scan range of \( m/z \) 312.0 – 372.0, a mass resolution of 70,000 (FWHM) at a scan rate of 1 Hz. The DART source was positioned 6.1 cm on the horizontal scale, 7 cm on the vertical scale with an angle of 45°, such that it is around 1 mm above the surface (Fig. S5). The distance from the surface to the ceramic tube is minimized by placing them at the edge of the moving rail so that maximum of the singly protonated UPy–CF\(_3\) and UPy–I ions (\( m/z \) 313.09029 and 370.99859 respectively) would enter the MS.

## 2. Synthesis

**2.1 General Remarks.** Unless stated otherwise, solvents and dry solvents like 2-propanol, dichloromethane, chloroform, DMSO, \( N \)-methylpyrrolidone and toluene were purchased from Sigma-Aldrich. Unless stated otherwise all of these chemicals were used without further purification.

**2.2. Reaction Handling.** Unless stated otherwise all non-aqueous reactions were performed in dried glassware under an atmosphere of argon. All flasks were equipped with rubber septa and reactants were handled using standard Schlenk techniques. Temperatures above the room
temperature refer to oil bath temperatures which were controlled by a thermostat. Reactions were magnetically stirred.

2.3. $^1$H-NMR spectra were recorded at room temperature on a Bruker AVB-400 spectrometer with $^1$H operating frequency of 400 MHz. Unless stated otherwise all spectra were recorded at room temperature in CDCl$_3$ and DMSO-$d_6$ and all chemical shifts are given in δ units relative to the residual solvent [central line of singlet: δ$_H$ = 7.27 ppm (CDCl$_3$) and 2.50, 3.33 ppm (DMSO-$d_6$)]. Analysis followed first order and the following abbreviations were used throughout: s = singlet, br. s. = broad singlet, d = doublet, t = triplet, q = quartet, quin = quintet, sxt = sextet, sept = sept, dd = doublet of doublet, dt = doublet of triplet, m = multiplet, mc = centred multiplet. Coupling constants (J) are given in Hertz (Hz).

2.4. $^{13}$C-NMR spectra were recorded at room temperature on a Bruker AVB-400 spectrometer with $^{13}$C operating frequency of 101 MHz. Unless stated otherwise all spectra were recorded at room temperature in CDCl$_3$ and DMSO-$d_6$ and all chemical shifts are given in δ units relative to the residual solvent [central line of triplet: δ$_C$ = 77.0 ppm (CDCl$_3$) and heptet δ$_C$ = 77.0 ppm (DMSO-$d_6$)]. The following abbreviation was used throughout: s = singlet, d = doublet, dd = doublet of doublet. If no coupling constants are given, the multiplicity refers to $^1$H-decoupled spectra.

2.5. Synthesis of UPy–Link, 1.

The synthesis of above was carried out according to a literature procedure.$^{51}$ Briefly, 6-methylisocytosine (2.0 g, 16.0 mmol) was added to 15 mL of DMSO and heated up to 170 °C
for 10 min. Once the solid dissolved, the oil bath was removed. 1,6-Hexamethylene diisocyanate (2.68 mL, 17.6 mmol) was added immediately to the flask under vigorous stirring. The mixture was quickly cooled using a water bath. A fine white solid precipitated upon cooling. The precipitate was collected and washed with excess acetone and dried under vacuum to obtain 3.50 g of a white solid (yield 75%). The $^1$H-NMR spectrum was in accordance to literature values.$^{32}$ The $^{13}$C NMR could not be obtained due to low solubility in NMR solvents even at high temperatures.


\[
\begin{align*}
\text{N} & \quad \text{N} \\
\text{N} & \quad \text{O}
\end{align*}
\]

The synthesis of above was carried out according to a literature procedure.$^{31}$ 6-Methylisocytosine (1.0 g, 8.0 mmol) was added to 15 mL of DMSO and heated up to 170 °C for 10 min. Once the solid dissolved, the oil bath was removed. 4-(Trifluoromethyl)phenyl isocyanate (1.3 mL, 8.8 mmol) was added immediately to the flask under vigorous stirring. The mixture was quickly cooled using a water bath. A fine white solid precipitated upon cooling. The precipitate was collected and washed with excess acetone and dried under vacuum to obtain 1.50 g of a white solid (yield 72%). The $^1$H-NMR spectrum was in accordance to literature values.$^{33}$ $^{13}$C NMR (600 MHz NMR, DMSO-$d_6$, 70 °C) $\delta$ = 162.0, 155.1, 151.5, 142.0, 125.7, 125.0, 118.9, 112.87, 103.34, 100.09 21.6.
2.7. Synthesis of UPy–I, 3.

The synthesis of above was carried by modification of a literature procedure.\textsuperscript{Sl} \textsuperscript{6-Methylisocytosine (1.0 g, 8.0 mmol) was added to 15 mL of DMSO and heated up to 170 °C for 10 min. Once the solid dissolved, the oil bath was removed. 4-Iodophenyl isocyanate (2.1 g, 8.8 mmol) was added immediately to the flask under vigorous stirring. The mixture was quickly cooled using a water bath. A fine white solid precipitated upon cooling. The precipitate was collected and washed with excess acetone and dried under vacuum to obtain 1.80 g of a white solid (yield 61%).}^{1}H NMR (400 MHz, DMSO-\textit{d}_6) \delta = 11.04 (s, 1H), 10.05 (s, 1H), 7.62 (d, J = 8.6 Hz, 2H), 7.36 (d, J = 8.6 Hz, 2H), 5.80 (s, 1H), 2.16 (s, 3H) \textsuperscript{13}C NMR (600 MHz NMR, DMSO-\textit{d}_6, 70 °C) \delta = 162.0, 155.1, 151.8, 137.2, 121.3, 116.37, 103.5, 100.1, 86.1, 21.7.
3. NMR data

- $f_1$ (ppm) values:
  - 2.72
  - 1.00
  - 2.01
  - 1.92
  - 1.31
  - 1.28
  - 2.17
  - 2.47
  - 3.27
  - 5.82
  - 7.63
  - 7.65
  - 7.73
  - 7.79
  - 10.16
  - 11.47

Chemical structure:

\[
\begin{align*}
\text{O} & \quad \text{CF}_3 \\
\text{N} & \quad \text{N} \\
\text{N} & \quad \text{N} \\
\text{H} & \quad \text{H} \\
\end{align*}
\]
4. Surface Preparation and Kinetics Determination

4.1 Preparation of phosphonic acid monolayers. 2×1 cm Al slides were sonicated in DCM for 15 min followed by wiping with lint-free cotton swabs (Texwipe, NC, USA) to remove the polymer protection layer on top and remove any residual glue. The surfaces were chemically activated by immersing in 1:1 (v/v) 37% HCl/MeOH mixture for 5 min, followed by washing with water and 2-propanol. The activated surfaces were then immersed into N₂ filled vials of 5 mM solution of 12-aminododecylphosphonic acid hydrochloride salt (C₁₂–NH₂ PA HCl salt) in 2-propanol, heated to 50 °C for 5 min, and then left undisturbed for 5 h at room temperature to obtain self-assembled monolayers. Thereafter, surfaces were taken out and sonicated successively for 5 min with 2-propanol, acetone and dichloromethane. The surfaces were then cleaned with dichloromethane, air dried and stored under argon atmosphere.

Scheme S1. Preparation of C₁₂–NH₂-terminated self-assembled monolayer on Al. (S1)
4.2 Preparation of UPy-terminated monolayers. UPy–Link (300 mg, 40 mM) was dissolved in 25 mL N-methylpyrrolidone (NMP) by sonication and heating followed by addition of DBTDL (45 µl, 0.4 mM). Amine-terminated Al chips were loaded onto a PTFE holder and stirred in this solution at 60 °C for 6h. The N1s/P2s ratio in XPS was used to optimize the stirring time and temperature. The samples were sonicated for 10 minutes successively with NMP, water, 2-propanol and acetone followed by drying under N\textsubscript{2} stream and storage under argon atmosphere.

Scheme S2. Preparation of UPy–Link terminated surfaces from C\textsubscript{12}–NH\textsubscript{2}-terminated monolayers. (S2)
4.3 Preparation of H-bonded dimers on the surface. UPy–CF$_3$ (7.8 mg, 1 mM) or UPy–I (9.2 mg, 1 mM) was dissolved in 25 mL toluene by sonication. UPy–Link terminated samples were loaded onto a PTFE holder and stirred in this solution at 25 ºC. To commence the kinetic studies, samples were taken out of the solution at different time points, sonicated in toluene for 5 min and dried under nitrogen stream. The samples were then directly used for different analysis or exchange experiments.

Scheme S3. Preparation of Link–UPy···UPy–CF$_3$ (S3) from UPy–Link termination (S2).

Scheme S4. Preparation of Link–UPy···UPy–I (S4) from UPy–Link termination (S2).
4.4 Functionality-independent UPy exchange. For exchange experiments, H-bonded dimer containing samples were allowed to react with a 1 mM solution of the incoming UPy in toluene at 25 °C or 50 °C followed by sonication for 1 min in toluene and drying under argon. The samples were then directly used for DART or XPS analysis.

Scheme S5. Functionality independent exchange of UPy on Al surface. (S3 to S4 and vice versa)

4.5 Kinetics of UPy–CF$_3$ attachment on surface. Equations S1–S3 describe the rate for the studied reaction (mol·cm$^{-2}$·s$^{-1}$), where $\Gamma_{UPy}$ is the density of surfacial UPy groups on the surface (mol·cm$^{-2}$) available to undergo H-bonding with its UPy counterpart in solution, and $k_2$ is the second-order rate constant (M$^{-1}$·s$^{-1}$). Since the amount of UPy in solution ([UPy (soln)] = 1 mM) is in very large excess compared to the amount of surfacial UPy ($\Gamma_{UPy}$ = ~18 pmol·cm$^{-2}$) it can be assumed to be essentially constant throughout the entire kinetic regime. Thus, the self-complementary UPy···UPy quadruple hydrogen bonding on a surface can be reduced to pseudo-first order kinetics, with rate constant, $k'$, where, $k' = k_2$· [UPy

Therefore, using the MS intensity data, from plots of \( \ln \left| \frac{I_t - I_\infty}{I_0 - I_\infty} \right| \) versus time (where \( I \) corresponds to the integrated EIC intensity at \( t = 0, t \) or \( \infty \) (completed reaction)), the resulting pseudo-first order rate constant \( k' \) can be obtained directly from the slope, as shown in equation (S3). Based on this pseudo-first order rate constant, the corresponding second-order rate constant \( k_2 \) can subsequently be calculated from equation (S5).

\[
v = k_2 [UPy (soln)] \Gamma_{UPy} = \frac{d\Gamma_{UPy}}{dt} \quad (S1)
\]

\[
v = k' \Gamma_{UPy} \quad (\because [UPy (soln)] \gg \Gamma_{UPy}) \quad (S2)
\]

\[
\ln \left( \frac{I_t - I_\infty}{I_0 - I_\infty} \right) = -k't \quad (S3)
\]

\[
k'(s^{-1}) = k_2 [UPy (soln)] \quad (S4)
\]

\[
k_2(M^{-1}s^{-1}) = \frac{k'}{[UPy (soln)]} \quad (S5)
\]
5. Supplementary Figures

**Supplementary Figure S1.** XPS wide scan of C_{12}-NH_{2} monolayers.

**Calculation of Atomic percentages:**

Theoretical N/P = 1

Observed N/P = 0.98 ± 0.3

Theoretical C/P = 12

**Observed C/P = 13 ± 0.5**
Supplementary Figure S2. GATR–FTIR spectra of Al surface terminated with C_{12–NH_2} (S1), UPy–Link (S2) and Link–UPy···UPy–CF_3 (S3) dimers.
Supplementary Figure S3. XPS wide scan of UPy–Link attachment.

Calculation of Surface Attachment from Atomic percentages:

For surface S1 the N/P ratio is equal to 1.

For surface S2 the N/P ratio at 100% covalent UPy binding is equal to 6.

Hence, if the degree of UPy binding is not 100%, the degree can be calculated from the experimentally determined N/P ratio, according to:

\[
\text{Conversion } S1 \rightarrow S2 = \frac{\left(\frac{N}{P}\right)_{\text{exp}} - 1}{6 - 1}
\]

Inserting an experimentally determined N/P ratio of 3.6 for surface S2 in the above equation leads to a conversion of 52%.
Supplementary Figure S4. Percentage completion for UPy–Link formation across several samples as determined by XPS.
### Supplementary Figure S5. Stacked XPS C1s narrow scan of surfaces S1, S2 and S3.

<table>
<thead>
<tr>
<th>Name</th>
<th>Pos.</th>
<th>FWHM</th>
<th>L.Sh.</th>
<th>Area</th>
<th>%Area</th>
</tr>
</thead>
<tbody>
<tr>
<td>N 1s</td>
<td>400.01</td>
<td>1.99</td>
<td>GL(30)</td>
<td>727.13</td>
<td>100.00</td>
</tr>
</tbody>
</table>
Supplementary Figure S6. XPS N1s narrow scan of UPy−Link attachment.
**Supplementary Figure S7.** Typical DART setup.
Supplementary Figure S8. Representative DART ion intensity EIC for Link–UPy···UPy–CF$_3$ dimers (S3). a) Top panel represents total ion current (TIC); bottom panel represents extracted ion chromatogram (EIC) ($m/z$ window 10 mmu around ion of interest). b) relative error between obtained $m/z$ and theoretical $m/z$ of ion of interest c) peak of ion of interest (UPy–CF$_3$).
Supplementary Figure S9. F/P ratio in XPS for Link–UPy···UPy–CF₃ formation over time (min).
Supplementary Figure S10. XPS wide scan of Link–UPy···UPy–CF₃ on surface with a) N/P and b) F/P ratios.
Calculation of Atomic percentages:

To calculate the maximum N/P ratio for surface S3, one should consider that 48% of the surface sites are amine-terminated, with N/P ratio of 1 (see Figure S3, page S19). If all UPy sites on the surfaces, which make up 52% of the surface, will dimerize, their N/P becomes 10. Hence, the maximum N/P ratio for surface S3 is: $0.48 \times 1 + 0.52 \times 10 = 5.68$.

Consequently, the actual degree of surface UPy dimerization is calculated by:

$$
Conversion_{S2\rightarrow S3} = \frac{(N/P)_\text{exp} - 3.6}{5.68 - 3.6}
$$

Inserting an experimentally determined N/P ratio of 4.3 for surface S3 in the above equation leads to a degree of UPy dimerization of 34%.

Similarly, based on the F/P ratio, also a degree of UPy dimerization can be calculated. As explained above, only 52% of the surface sites are capable of binding UPy–CF3. Hence, the maximum F/P ratio (at 100% dimerization) is equal to $0.52 \times 3 = 1.56$. Consequently, the actual degree of surface UPy dimerization is calculated by:

$$
Conversion_{S2\rightarrow S3} = \frac{(F/P)_\text{exp}}{1.56}
$$

Inserting an experimentally determined F/P ratio of 0.6 for surface S3 in the above equation leads to a degree of UPy dimerization of 38%.
**Supplementary Figure S11.** Attenuation of Al2p intensity in XPS on formation of C_{12}–NH_{2}, UPy–Link and Link–UPy···UPy–CF_{3} dimers.
**Supplementary Figure S12.** XPS wide scan of control samples reacted with UPy–CF₃.

**Calculation of Atomic percentages:**

Theoretical N/P ratio ≤ 4

Observed N/P ratio = $1 \pm 0.1$
Supplementary Figure S13. DART measurement of control samples reacted with UPy–CF₃.
**Calculation of Atomic percentages:**

Theoretical N/P (100% recovery) = 3.6

Observed N/P = 3.3 ± 0.2

**Supplementary Figure S14.** XPS wide scan of UPy–CF₃ removal by sonication in acetone and subsequent reassembly.
Supplementary Figure S15. XPS wide scan of Link–UPy···UPy–I on surface.

Calculation of Atomic percentages:

Theoretical I/P = 0.6

Observed I/P = 0.2 ± 0.03

Fraction of H-bonded surface-bound UPy–I = 35 ± 5%
Supplementary Figure S16. XPS I3d narrow scan of Link–UPy···UPy–I on surface.
**Supplementary Figure S17.** DART measurement of UPy–CF₃ displacement with UPy–I showing both ionized species. a) Top: total ion current (TIC); middle: extracted ion chromatogram (EIC) of UPy–CF₃; bottom: extracted ion chromatogram (EIC) of UPy–I. b) relative error between obtained m/ and theoretical m/z. c) peak of ion of interest. (UPy–I).
**Supplementary Figure S18.** XPS wide scan of UPy–CF$_3$ displacement by UPy–I.

**Calculation of Atomic percentages after exchange:**

Theoretical F/P = 0

Observed F/P = 0.3 ± 0.04

**Supplementary Figure S19.** F/P ratio in XPS for UPy–CF$_3$ displacement by UPy–I.
Supplementary Figure S20. XPS wide scan of UPy–CF$_3$ displacement by UPy–I at 50 °C.

Calculation of Atomic percentages after exchange:

Theoretical I/P = 0.6

Observed I/P = 0.21 ± 0.04

% UPy–I on surface = 35 ± 5%
Supplementary Figure S21. DART–HRMS Scan of UPy–CF₃ displacement by UPy–I at 50 °C. a) top: total ion current (TIC) middle: EIC of UPy–CF₃ bottom: EIC of UPy–I. b) peak of ion of interest (UPy–CF₃) c) peak of ion of interest (UPy–I).
Supplementary Figure S22. DART kinetics of UPy exchange at a surface.
Supplementary Figure S23. XPS wide scan of Link–UPy···UPy–CF₃ (S3) surfaces after stirring in toluene at 80 °C for 24 h.

Supplementary Figure S24. XPS wide scan of Link–UPy···UPy–CF₃ (S3) surfaces after stirring in toluene at 80 °C for 48 h.
Supplementary Figure S25. XPS wide scan of Link–UPy···UPy–CF₃ (S3) surfaces after stirring in toluene at 80 °C for 120 h.

Calculation of Atomic percentages

Initial F/P = 0.7

Observed F/P (after 120 h) = 26.34/73.76 = 0.36

% UPy remaining on surface = 0.36/0.7 = 52%
Supplementary Figure S26. Plot of % CF₃–UPy removed (F/P in XPS) from S3 surfaces after stirring in toluene at 80 °C vs time (h).

Rate Constant (80 °C) = 0.016 h⁻¹ = 4.4 × 10⁻⁶ s⁻¹

Rate (25 °C) = $k_{\text{off}} \sim 10^{-7}$ s⁻¹

$k_{\text{on}}$ (pseudo-first order) = $22 \times 10^{-4}$ s⁻¹

$k_{\text{on}}$ (second order for 1 mM UPy in solution) = $22 \times 10^{-4}$ s⁻¹ / $10^{-3}$ M = $2.2$ M⁻¹·s⁻¹

$K = k_{\text{on}}$ (second order) / $k_{\text{off}} = 2.2 \times 10^7$ M⁻¹
6. Supplementary Tables

**Table S1.** Rate constants for UPy exchange (25 °C in toluene) at the surface.

<table>
<thead>
<tr>
<th>UPy displacement</th>
<th>Increasing/ Decreasing signal</th>
<th>Rate ($\times 10^{-4}$ s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CF$_3$–UPy to UPy–I</td>
<td>Decrease in CF$_3$–UPy</td>
<td>4.0 ± 0.4</td>
</tr>
<tr>
<td></td>
<td>Increase in UPy–I</td>
<td>4.3 ± 0.3</td>
</tr>
<tr>
<td>UPy–I to CF$_3$–UPy</td>
<td>Decrease in UPy–I</td>
<td>3.8 ± 0.3</td>
</tr>
<tr>
<td></td>
<td>Increase in CF$_3$–UPy</td>
<td>3.9 ± 0.2</td>
</tr>
</tbody>
</table>
7. Material Studio Data

7.1 Surface preparation. Al oxide (Al$_2$O$_3$) surface in bulk. All colors used are standard throughout (Grey = C, purple = P, white = H, pink = Al, red = O, blue = N)
Al₂O₃ were cleaved along (h k l) = (−1 0 0) to build oxidic aluminium surfaces.

Thickness fractional = 1

Thickness (Å) = 4.121

Cap bonds on Top = O( oxygen)

**Vacuum Slab Build Dimensions**

Vacuum orientation C (axis)

Vacuum thickness = 74.5048 Å

Crystal thickness = 80.00 Å
7.2 Scheme for monolayer attachment (2×4)

- Amine monolayer
- No monolayer
7.3 Example of 8×16 cell used for packing energy calculation (50% coverage)

7.4 Example of 8×16 cell used for packing energy calculation (50% coverage).
7.5 Plot of energies of various coverages plotted (kcal/mol) vs percentage monolayer coverage (%).

<table>
<thead>
<tr>
<th>% Coverage</th>
<th>Packing energy (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>78.1</td>
<td>23.61</td>
</tr>
<tr>
<td>65.6</td>
<td>-3.34</td>
</tr>
<tr>
<td>50.0</td>
<td>-7.75</td>
</tr>
<tr>
<td>37.5</td>
<td>-4.81</td>
</tr>
<tr>
<td>25.0</td>
<td>-4.78</td>
</tr>
</tbody>
</table>
7.6 Scheme for Link–UPy attachment in a 8×16 cell (on 50% monolayer coverage)
62.5%

- Black circle = Amine termination
- Red circle = No monolayer
- Light blue circle = Hex UPy
7.7 Representative images for initial 62% Link–UPy attachment in a $8 \times 16$ cell (on 50% monolayer coverage).

7.8 Molecular modelling (MM) results using Forcite module (NVT ensemble, PCFF) on Link–UPy attachment on aluminum surface (62% coverage). Extensive H-bonding between adjacent surface-bound UPy moieties can be seen.
8. References

