## Fabrication of a nanoparticle gradient substrate by thermochemical manipulation of an ester functionalized SAM<sup>†</sup>

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The hydrolysis of methyl ester (-CO<sub>2</sub>Me) and *tert*-butyl ester (-CO<sub>2</sub>Bu) functionalized SAMs as a function of subphase temperature and pH is described. Contact angle measurements show that the methyl ester functionalized monolayer does not hydrolyse in pH 1-13 aqueous solutions heated up to 80 °C. In contrast, the  $-CO_2^{t}Bu$  functionalized monolayer hydrolysed below pH 5. The rate and the extent of the hydrolysis were dependent on the temperature and pH of the aqueous solution. Using the Cassie equation, the activation energy for the hydrolysis of  $CO_2^{t}Bu$ phenyl functionalized SAM was determined as 75  $\pm$  7 kJ mol<sup>-1</sup> from the contact angle measurements. Furthermore, the adhesion properties of -CO<sub>2</sub><sup>t</sup>Bu and -COOH functionalized SAMs were investigated by depositing -NR<sub>2</sub> and -COOH functionalized polystyrene nanoparticles onto the surfaces at pH 3 and 9. By AFM, it was observed that the particles bind preferentially to the -COOH functionalized SAM and the adhesion was pH dependent, with the largest coverage being observed at pH 3. Using the acquired understanding of the hydrolysis of -CO<sub>2</sub><sup>t</sup>Bu functionalized SAM and the particle adhesion properties, a simple and facile approach towards fabricating a particle density gradient on this surface is demonstrated. An acid gradient SAM (20 mm long) was prepared by mounting one end of a  $-CO_2^{t}Bu$  functionalized SAM onto the hot side of a Peltier element (80 °C) in pH 1 aqueous solution. The substrate was subsequently immersed into a colloidal solution of  $-NR_2$  functionalized polystyrene nanoparticles, removed and rinsed. By AFM, the particle density was shown to be dependent on the surface coverage of -COOH moieties of the underlying SAM. The density started at 104 particles  $\mu m^{-2}$  on the hydrolysed end down to 0 particles  $\mu m^{-2}$  on the non-hydrolysed end.

#### **1** Introduction

The ability to immobilise single molecules, molecular aggregates or nanoparticles onto selective sites on surfaces of metals and semiconductors is of major interest in nanotechnology as it is seen as a possible route towards nanofabrication.<sup>1</sup> The combination of top-down lithography processes with bottom-up self-assembly processes termed "precision chemical engineering"<sup>2</sup> is seen as a possible route towards nanofabrication. The approach involves the fabrication of ultrathin films followed by chemical manipulation of the surfaces by

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lithographic techniques such as electron beam (e-beam),<sup>3-5</sup> X-rays,<sup>6,7</sup> UV/Vis<sup>8</sup> irradiation and finally self-assembling nanomaterials on to the modified surfaces.

Self-assembled monolayers (SAMs) provide a simple route towards functionalising surfaces of metals,<sup>9</sup> insulators<sup>10</sup> and semiconductors.<sup>11</sup> The terminal groups can be tailored to provide control over the surface properties, and thus provide the necessary control required over the reactions which take place on the surface, hence allowing controlled fabrication of three-dimensional structures. For instance, there have been several groups who have used nitro functionalized SAMs as building blocks towards fabricating three-dimensional structures, *via* selectively inducing chemical modification of the nitro moieties to amine moieties by irradiating regions with an e-beam,<sup>4,5</sup> or X-rays<sup>7</sup> and then performing coupling reactions,<sup>4</sup> or by absorbing Au nanoparticles<sup>5</sup> on the modified surfaces to obtain three-dimensional structures.

Recently, chemical gradient SAMs, which exhibit a continuous spectrum of surface properties,<sup>12–16</sup> have attracted enormous interest, as such surfaces reduce the number of substrates required to perform particle adhesion studies, catalytic studies,<sup>12</sup> combinatorial studies,<sup>13</sup> protein attachment,<sup>14,15</sup> cell adhesion and cell mobility.<sup>16</sup> Since Elwing *et al.*<sup>14</sup> first introduced the concept, there have been a number of approaches reported for fabricating such SAMs. These methods either involve the controlled diffusion of surfactants

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onto a substrate,<sup>14,17,18</sup> controlled immersion of a substrate into a surfactant solution,<sup>19</sup> applying an electrochemical potential to a substrate during adsorption,<sup>12,20</sup> using microfluidic devices,<sup>21</sup> chemical manipulation<sup>13,15,16,22–26</sup> of ultrathin films by radio frequency plasma discharge,<sup>22</sup> corona discharge treatment,<sup>23</sup> UV light<sup>25</sup> and grafting.<sup>26</sup> Recently, Shosky and Schönherr<sup>13</sup> demonstrated a simple approach for obtaining gradient SAMs by heating an aliphatic *tert*-butyl ester functionalized SAM with the aid of a Peltier element, which was used as a heat pump. One end of the substrate (2.5 cm long) was mounted onto a Peltier element and heated to the required temperature. A temperature gradient was established along the substrate from the set temperature on the hot end to room temperature on the cool end. When placed in an acidic liquid cell, the extent of hydrolysis along the substrate progressed from 100% hydrolysis at the hot end to 0% hydrolysis at the cool end. The approach was developed to determine the kinetic studies for chemical reactions on ultrathin films.

In this paper, a novel, simple and facile approach for fabricating nanoparticle gradient SAMs is described. Using the approach described by Shosky and Schönherr<sup>13</sup> an acid gradient SAM is produced by hydrolysing a *tert*-butyl ester functionalized SAM with the aid of a Peltier element followed by deposition of the particles (Fig. 1). The –COOH moieties provide the active sites for the binding of the particles, as it has previously been demonstrated that –COOH functionalized SAMs are amenable to particle adhesion,<sup>27</sup> as well as protein attachment<sup>28</sup> and cell adhesion.<sup>29</sup> Such particle gradient surfaces provide the opportunity to study arrays of surface



Fig. 1 Schematic representation of the approach used for the fabrication of the nanoparticle gradient substrate: (a) hydrolysis of ester functionalized monolayer ( $-CO_2R$ ) using a Peltier element, (b) acid gradient SAM prepared, (c) substrate immersed in colloidal solution, and (d) nanoparticle gradient.



Fig. 2 Molecular structures of the molecules used in the investigation.

properties such as optoelectronics and catalysis as a function of particle density on a single substrate, which would provide valuable information for preparing future nanodevices that contain nanoparticles. Previously, there have been only a few examples reported where gradient nanoparticle substrates have been prepared. Such substrates were prepared either by immersion of a Si/SiO2 substrate into a colloidal solution of nanoparticles as a function of immersion time<sup>19</sup> or by adsorbing citrate Au nanoparticles on a gradient (3-aminopropyl)triethoxysilane (APTES) SAM on a silica substrate, where the gradient SAM was prepared by vapour deposition of APTES on a Si/SiO<sub>2</sub> substrate as a function of exposure time along the substrate.<sup>17</sup> There are two major differences in our approach compared to previously reported approaches. Firstly the particle gradient is fabricated on a Au substrate, and secondly it is fabricated on a complete monolayer containing two functional moieties at each terminus of the SAM, hence providing the possibility to further chemically manipulate the ester moieties for constructing additional three-dimensional structures. Furthermore, to optimise the conditions required for the hydrolysis of -CO<sub>2</sub><sup>t</sup>Bu functionalized SAMs prepared from 4-(6-mercapto-hexyloxy) benzoic acid tert-butyl ester (**MHBTE**, I) (Fig. 2), the hydrolysis of  $-CO_2^{t}Bu$  as a function of pH and temperature is investigated. Although there have been a number of papers reporting the hydrolysis of

bulky ester functionalized SAMs such as -CO2tBu13,30 and hydroxysuccinimide ester,<sup>31</sup> to our knowledge the hydrolysis behaviour of the smaller esters such as methyl ester (-CO<sub>2</sub>Me) has not been reported. As the esters are less bulky the packing in the monolayer will be different compared to the bulkier ester moieties, and also the mechanisms for the hydrolysis of the ester moieties are different, which may influence the hydrolysis behaviour in the SAM, where the molecules are confined in a quasi-crystalline structure.<sup>32,33</sup> Thus, in this paper the hydrolysis behaviour of a -CO<sub>2</sub>Me functionalized SAM prepared by 4-(6-mercapto-hexyloxy) benzoic acid methyl ester (MHBME, II) (Fig. 2) is studied and compared to the  $-CO_2^{t}Bu$  functionalized (MHBTE, I) SAM as a function of pH and temperature. Finally, to optimise the adhesion of particles on the acid gradient SAM, the attachment of tertiary amine functionalized and acid functionalized polystyrene nanoparticles on both MHBTE (I) and acid functionalized SAM 4-(6-mercaptohexyloxy) benzoic acid (MHBA, III) SAMs (Fig. 2) in acidic and basic colloidal solutions is investigated.

#### 2 Results and discussion

#### 2.1 Synthesis of the arylthiols (I-III)

The thiols (I–III) were synthesised from commercially available 4-hydroxybenzoic acid (Scheme 1). The first step was the esterification of 4-hydroxybenzoic acid (1) to the corresponding esters (**2a** and **2b**). **2a** was obtained by DCC coupling with <sup>1</sup>BuOH in THF,<sup>34</sup> whereas 4-hydroxy-1-methyl benzoate (**2b**) was obtained under methanolic acidic (H<sub>2</sub>SO<sub>4</sub>) conditions. The phenol derivatives (**2a** and **2b**) were alkylated with 1,6-dibromohexane in the presence of a base (K<sub>2</sub>CO<sub>3</sub>) to obtain **3a** and **3b**.<sup>35</sup> Finally, the thiol moiety was introduced through the reaction of **3a** and **3b** with thiourea to form the intermediate isothiouronium salt, which was cleaved under basic conditions (NaOH) to yield the thiols (I–II).<sup>36</sup> The acid (III) was formed by addition of two more equivalents of aqueous NaOH to II.



Scheme 1 Synthesis of the aryl based thiols.

SAM	Contact angle measurements				
	Observed		Literature		
	$\theta_{\rm a}/^{\circ}$	$ heta_{ m r}$ / $^{\circ}$	$ heta_{ m a}$ / $^{\circ}$	SAM thickness <sup>a</sup> /nm	Molecular length <sup>b</sup> /nm
MHBTE (I) MHBME (II) MHBA (III)	$     \begin{array}{r} 89 \pm 1 \\     64 \pm 1 \\     10 \pm 3     \end{array} $	$\begin{array}{cccc} 78 \ \pm \ 1 \\ 48 \ \pm \ 1 \\ 0 \end{array}$	$89^{30} \\ 65^{37} \\ \sim 10^{\circ} \ ^{37-39}$	$\begin{array}{c} 1.31 \ \pm \ 0.04 \\ 1.60 \ \pm \ 0.12 \\ 1.40 \ \pm \ 0.10 \end{array}$	1.79 1.64 1.45
<sup>a</sup> The SAM thickne	ss obtained from ell	lipsometry <sup>b</sup> The mol	ecular length obtained f	rom Chem 3D software	

Table 1 Wetting properties (water contact angles) and monolayer thickness

#### 2.2 Preparation of the SAMs

The SAMs were formed by immersion of the Au substrates in 1 mM solutions of I–III in EtOH (HPLC grade) for 24 h. After 24 h the Au substrates were thoroughly rinsed with EtOH (HPLC grade) and dried with a stream of  $N_2$ .

#### 2.3 SAM characterisation

The SAMs were characterised by water contact angle measurements, X-ray photoelectron spectroscopy (XPS) and ellipsometry. As expected the **MHBME** (II) SAM is more hydrophilic than **MHBTE** (I), which is presumably due to the bulkier *tert*-butyl moiety screening the influence of the polar ester from the monolayer surface. The monolayer formed from **MHBA** (III) is extremely hydrophilic (advancing angle  $\theta_a$   $10 \pm 2^\circ$  and receding angle  $\theta_r \sim 0^\circ$ ) and exhibits similar contact angles to literature values.<sup>37–39</sup> The monolayer thicknesses obtained for the SAMs are smaller than the molecular length of the molecules as shown in Table 1. The discrepancy between the SAM thicknesses and the molecular lengths suggests that the monolayers are tilted, which is typically found for alkanethiol molecules adsorbed onto gold.<sup>40</sup> The

XPS survey spectra for **MHBTE** (I), **MHBME** (II) and **MHBA** (III) SAMs show the presence of peaks at binding energies 284, 400, 581 and 162 eV, which are indicative of the presence of C, N, O and S, respectively (the XPS survey spectra are shown in ESI,† Fig. S1).

#### 2.4 pH and temperature dependence of the hydrolysis

**2.4.1 pH dependence of the hydrolysis.** The hydrolysis of **MHBTE (I)** and **MHBME (II)** SAMs was studied over a pH range of 1–13. The SAMs were immersed in pH 1–13 aqueous solutions for 5 h at 20 °C and 80 °C. At 20 °C, neither ester showed any significant change in  $\theta_a$  and  $\theta_r$  over the pH range (Fig. 3a and b), suggesting little or no hydrolysis had taken place. At the elevated temperature of 80 °C, for the  $-CO_2^{t}Bu$  functionalized SAM (Fig. 3c) it can be seen from pH 13 down to pH 5 there is no change in the contact angle, but below pH 5 the contact angle drops as a function of pH down to  $\theta_a 15^\circ$  and  $\theta_r \sim 0^\circ$  at pH 1. These lower contact angles are characteristic for -COOH functionalized monolayers, and are similar to the contact angle observed for **MHBA (III)**. Thus, the hydrolysis of the ester is near to complete at pH 1. It should be noted that



(b) MHBME (II) SAM at room temperature 100 90 Advancing angle □ Receding angle 80 Contact angle / 70 60 50 40 30 20 10 0 1 2 3 5 7 11 13 Initial 9 pH (d) MHBME (II) SAM at 80 °C 100 Advancing angle □ Receding angle 90 80 Contact angle / ° 70 60 50 40 30 20 10 0 Initial 1 2 3 5 7 9 11 13 pН

**Fig. 3** Contact angle measurements taken after immersing (a) **MHBTE (I)** SAM at room temperature, (b) **MHBME (II)** SAM at room temperature, (c) **MHBTE (I)** SAM at 80 °C and (d) **MHBME (II)** SAM at 80 °C in aqueous solution with pH ranging from 1–13 for 5 h.

alkanethiol-Au SAMs are known to desorb at elevated temperatures,<sup>41</sup> and therefore in order to ensure that the change in wetting behaviour was due to a chemical change and not to desorption, the thickness of the modified SAM was determined by ellipsometry and the chemical composition was determined by XPS. The monolayer thickness was determined as  $1.58 \pm 0.10$  nm, which is comparable to the **MHBA (III)** SAM thickness ( $1.40 \pm 0.10$  nm). Furthermore, the survey spectra for the hydrolysed **MHBTE (I)** SAM reveal the presence of C (1s), S (2p) and O (1s) (see ESI,† Fig. S2). Hence, the change in the wetting properties of the surface is due to the hydrolysis of the ester. In the case of the  $-CO_2Me$  functionalized SAM there is no change in the contact angle (Fig. 3d), suggesting no hydrolysis had taken place in either acidic or basic medium.

To summarise, at 80 °C, hydrolysis only takes place on the MHBTE (I) SAM in acidic conditions (pH < 5), whereas no hydrolysis was observed on the MHBME (II) SAM under either acidic or basic conditions. One can postulate that the lack of reactivity of the -CO2Me functionalized SAM relative to the -CO<sub>2</sub><sup>t</sup>Bu functionalized SAM is due to the different types of mechanism that are in operation. The hydrolysis of CO<sub>2</sub>Me esters requires carbonyl oxygen protonation, followed by attack of water on the electrophilic carbonyl carbon atom (A<sub>AC</sub>1 mechanism).<sup>32,33</sup> However, the hydrolysis of CO<sub>2</sub><sup>t</sup>Bu esters does not require the attack of a nucleophile water, as a stable tert-butyl cation can be lost (AAL1 mechanism) which subsequently loses H<sup>+</sup> and forms gaseous isopropene.<sup>32,33</sup> Thus, one can envisage that in the quasi-crystalline SAM it is difficult for nucleophilic water to penetrate the SAM, and thus, the CO<sub>2</sub>Me ester SAM resists hydrolysis.

2.4.2 Temperature dependence of the ester hydrolysis. It has already been demonstrated that the hydrolysis of MHBTE (I) in pH 1 aqueous solution is temperature sensitive, as hydrolysis was achieved at 80 °C and no hydrolysis was noticeable at 20 °C. However, for the proposed preparation of an acid gradient SAM, we require the hydrolysis to be progressive between temperatures 20–80 °C, therefore, the hydrolysis of MHBTE (I) SAM over four temperatures (35, 44, 50 and 65 °C) in pH 1 aqueous solution was investigated (Fig. 4). It was observed that the hydrolysis is progressive over the temperature range 35–80 °C and contact angle measurements show no evidence of hydrolysis taking place below 35 °C. From the pH and temperature studies it has been



Fig. 4 The hydrolysis of MHBTE (I) SAM as a function of temperature.

demonstrated that the extent of the hydrolysis on **MHBTE** (I) SAM can be controlled by pH and temperature.

## 2.5 Partial hydrolysis of MHBTE (I) SAM using the Peltier element

**2.5.1 Determination of the temperature gradient.** The experimental set-up for the preparation of the gradient SAM is shown in Fig. 5. One end of the Au substrate was mounted onto the Peltier element (5 mm) with the setpoint (0 mm) being 2 mm from the edge which was mounted on the Peltier element. The temperatures along the substrate were taken at increments of 2 mm beginning from the setpoint using a thermocouple that was attached to a thermocouple module. The hot end of the substrate was heated to 80 °C, because preliminary studies showed complete hydrolysis of the  $-CO_2$ <sup>t</sup>Bu functionalized SAM was obtained in pH 1 solution heated at 80 °C for 5 h. The temperature gradient along the substrate is shown in Fig. 6, which also illustrates that the gradient is stable over 5 h.

**2.5.2 Determining the extent of the hydrolysis on the MHBTE** (I) SAM. All the contact angles reported from now are static contact angles. The contact angles were determined as static contact angles rather than dynamic contact angles to eliminate the risk of the water droplet expanding onto the next measuring point. The static contact angle for MHBTE (I) SAM was determined as  $88 \pm 1^{\circ}$  and MHBA (III) SAM it was determined as  $10 \pm 2^{\circ}$ .

The change in the contact angles along the substrate after one end of the **MHBTE** (I) has been heated to 80 °C by a Peltier element in a cell containing pH 1 aqueous solution for



Fig. 5 Schematic representation of the experimental setup used for preparing the acid gradient SAM.



Fig. 6 The temperature gradient along the MHBTE (I) SAM between the hot end and cold end of the substrate over 300 min.

30, 60, 180 and 300 min is shown in Fig. 7a. The hydrolysis is progressive from 0 to 10 mm. After 10 mm the contact angles plateau with the static contact angles measured as  $88-89^{\circ}$ . These data are in good agreement with the contact angle observed from the temperature study where no change in  $\theta_a$  was seen when hydrolysing the **MHBTE** (I) SAM at 35 °C.

In addition, at the setpoint (0 mm) the static contact angle is  $32 \pm 2^{\circ}$ , which suggests that the hydrolysis is not complete.

2.5.3 Determination of the activation energy  $(E_{a})$ . Bimolecular reactions are defined as second order reactions with the rate of reaction dependent on the concentration of the two reactants and the second order rate constant. In the case of the acid-catalysed hydrolysis reaction, the rate of reaction is dependent on the concentration of  $H^+$  ([ $H^+$ ]) and MHBTE (I) ([MHBTE]) as shown in ESI<sup>†</sup> equation (1). The second order rate constants (k) obey the Arrhenius equation (see ESI<sup> $\dagger$ </sup> equation (2)).<sup>11,42</sup> If k is known for a number of temperatures,  $E_{\rm a}$  for the reaction can be determined. According to previously reported studies on the hydrolysis of ester terminated SAMs, the hydrolysis is shown to follow a pseudo-first-order reaction. If [H<sup>+</sup>] is much larger than [MHBTE], [H<sup>+</sup>] can be regarded as a constant and hence  $k[H^+] \sim k'$  (pseudo-first-order rate constant), hence leaving the rate only dependent on [MHBTE] (see ESI<sup> $\dagger$ </sup> equation (3)). k' can be determined by integrating equation (3) (see ESI<sup> $\dagger$ </sup> equation (4)) from which k can be obtained.

Using the Cassie equation (see ESI† equation (5)) the extent of the hydrolysis can be determined from the contact angle.<sup>43</sup>



Fig. 7 (a) Static contact angle measurements along the substrate after hydrolysis of the **MHBTE** (I) SAM in pH 1 aqueous solution at 80 °C for 30, 60, 180 and 300 min, (b)  $\chi_{tbu}$  along the substrate determined from the static contact angle measurements using the Cassie equation, (c) the linear relationship between  $\ln(\chi_{tbu})$  and the reaction time (the lines are least-square fits) and (d) the linear relationship between  $\ln k'$  versus the inverse of the temperature.

The static contact angles along the substrate after reaction times 30, 60, 180 and 300 min are shown in Fig. 7a. It can be observed that the static contact angle measurements show that there are only significant changes in the contact angle along the first 8 mm of the SAM, after which point there is no sign of hydrolysis taking place after 30, 60, 180 and 300 min. At the higher temperatures the contact angle decreases more rapidly, which indicates a faster rate of reaction. The surface coverage for the  $-CO_2^{t}Bu$  functionalized monolayer ( $\chi_{tbu}$ ) along the substrate during the hydrolysis determined from the Cassie equation is shown in Fig. 7b.

Fig. 7c shows the natural logarithm of  $\chi_{tbu}$  plotted against reaction time; the linear relationship between the variables reaffirms that the hydrolysis reaction of **MHBTE** (I) in the conditions investigated is pseudo-first order. The slopes are least square fits that have  $R^2$  values in the range of 0.98–1. From the determined k' for the five temperatures investigated, the k values were determined by multiplying the values with [H<sup>+</sup>], which was 0.1 M. The k values are shown in ESI† Table S1. As expected, k increases with increasing temperature.

The second-order rate constants obtained from Fig. 7c are linearised according to the Arrhenius equation as shown in Fig. 7d. From the gradient of the plot in Fig. 7d,  $E_a$  for the hydrolysis of MHBTE (I) in aqueous pH 1 solution was determined as 75  $\pm$  7 kJ mol<sup>-1</sup>. Previously,  $E_{\rm a}$  for the acid catalysed hydrolysis of -CO2<sup>t</sup>Bu functionalized SAM determined by the use of the Cassie equation was reported as 28 kJ mol<sup>-1</sup>.<sup>13</sup> However, this was for an aliphatic *tert*-butyl ester and not an aromatic tert-butyl ester. As the initial step in the RCO<sub>2</sub><sup>t</sup>Bu ester hydrolysis is the protonation of the carbonyl moiety, we postulate that the difference between the  $E_a$  values may be due to the difference in the p $K_a$  values of the protonation of the respective esters. The  $pK_a$  of  $CO_2^{t}Bu$ aliphatic is reported as -6.5,<sup>44</sup> whereas the pK<sub>a</sub> of the protonation of  $CO_2^{t}Bu$ -phenyl is reported as -7.4.<sup>44</sup> Hence, the protonation of CO<sub>2</sub><sup>t</sup>Bu-phenyl is more difficult. Thus, it would be expected that the  $E_a$  value of  $CO_2^{t}Bu$ -phenyl would be larger than that for the CO<sub>2</sub><sup>t</sup>Bu-aliphatic functionalized SAM, as indeed is found to be the case.

## 2.6 Adhesion of functionalized nanoparticles on MHBTE (I) and MHBA (III) SAMs

To optimise the particle adhesion on the acid gradient SAM, two types of nanoparticles were deposited on the **MHBTE** (I) and **MHBA** (III) SAMs at pH 3 and 9 using unbuffered aqueous solutions containing:

(i) -COOH functionalized polystyrene latex (COOH-PL) nanoparticles (diameter: 40 nm);

(ii)  $-NR_2$  functionalized polystyrene latex (NR<sub>2</sub>-PL) nanoparticles (diameter: 60 nm).

These nanoparticles were chosen to utilise electrostatic interactions between the  $-COOH/COO^-$  functionalized surface and the nanoparticles. Particle attachment was studied at two different pH values (3 and 9), so that the protonated as well as the deprotonated surfaces (*i.e.* -COOH and  $-COO^-$ , respectively) could be investigated.

The particles were deposited onto the SAMs by immersing the SAMs in an aqueous solution of the particles at pH 3 and 9



**Fig. 8** Tapping mode AFM topography images of SAMs, after immersion in colloidal solution of COOH-PL nanoparticles: (a) on the **MHBTE (I)** SAM at pH 3, (b) on the **MHBTE (I)** SAM at pH 9, (c) on the **MHBA (III)** SAM at pH 3 and (d) on the **MHBA (III)** SAM at pH 9.

for 2 h, followed by rinsing with UHQ H<sub>2</sub>O and drying with N<sub>2</sub>. The surfaces were then analysed by AFM (an area of  $5 \times 5 \ \mu m^2$  was scanned).

2.6.1 Attachment of COOH-PL nanoparticles onto the SAMs. The particles were shown to selectively bind to the MHBA (III) SAM at pH 3 solution relative to MHBA (III) SAM at pH 9 and to MHBTE (I) SAM at both pHs as shown in Fig. 8a-d. The particle density was determined by visually counting the number of particles on the AFM images.<sup>45</sup> The particle density on MHBA (III) SAM at pH 3 was observed as 29 particles  $\mu m^{-2}$  (Table 2), whereas at pH 9 (COO<sup>-</sup> functionalized SAM) the particle density was 0 particles  $\mu m^{-2}$ . The particle density on MHBTE (I) SAM at pH 3 is much lower at 1.9 particles  $\mu m^{-2}$  and at pH 9 is 0 particles  $\mu m^{-2}$ . The discrepancy in the particle density on both substrates and at the different pHs can be rationalised by considering the intermolecular interactions between the functionalized surface and the nanoparticles. The -COOH functionalized SAM and the COOH-PL have complementary groups which can bind through hydrogen bonding at low pH, whereas the -CO<sub>2</sub><sup>t</sup>Bu moiety is a relatively hydrophobic group, and thus has less affinity for the -COOH/COO<sup>-</sup> moiety on the nanoparticles. Therefore, it would be expected that the COOH-PL nanoparticles would preferentially bind to the -COOH functionalized

Table 2Particle density on the MHBTE (I) and MHBA (III) SAMsafter being immersed in colloidal solution of NR2-PL nanoparticles atpH 3 and 9

	pН	Particle density/particles $\mu m^{-2}$		
SAM		COOH-PL	NR <sub>2</sub> -PL	
–COOH	3	29.0	104.0	
t	9	0	1.1	
–CO <sub>2</sub> 'Bu	3	1.9	0.3	
	9	0	0.1	

surface over the  $-CO_2^{t}Bu$  functionalized surface at low pH. The selective binding of the COOH-PL to the -COOH functionalized surface from pH 3 solution compared to pH 9 solution can be explained by referring to the p $K_a$  of the -COOH moiety. In free solution the p $K_a$  of a carboxylic acid is 4–5,<sup>46,47</sup> however, numerous studies on determining the p $K_a$  of -COOH moieties at the terminus of SAMs have reported it to be higher than in free solution (p $K_a$  5–8).<sup>48</sup> Hence, the p $K_a$  of the **MHBA** (**III**) SAM lies most probably between 4–8. Thus, at pH 3 both the monolayer and the COOH-PL particles will be near to fully protonated (COOH), and thus, the particles can bind to the surface through hydrogen bonding, whereas at pH 9 the COOH moieties in the monolayer and the particles will be near to fully deprotonated. The anionic charges will repel each other, and thus the particles will not attach at pH 9.

2.6.2 Attachment of NR<sub>2</sub>-PL nanoparticles onto the SAMs. Similar behaviour is observed for the NR<sub>2</sub>-PL nanoparticles. They show a preference for attachment on the MHBA (III) SAM at pH 3 relative to MHBA (III) SAM at pH 9 and MHBTE (I) SAM at both pHs as shown in Fig. 9a-d. The particle density on the -COOH functionalized surface at pH 3 is observed as 104 particles  $\mu m^{-2}$  (Table 2), whereas the particle density at pH 9 is 1.1 particles  $\mu m^{-2}$ . The particle densities on the -CO<sub>2</sub><sup>t</sup>Bu functionalized surface at pH 3 and 9 were 0.3 particles  $\mu m^{-2}$  and 0.1 particles  $\mu m^{-2}$ , respectively. We postulate that the selective binding to the -COOH over -CO<sub>2</sub><sup>t</sup>Bu functionalized SAMs at pH 3 is due to the NR<sub>2</sub>-PL particle being in the protonated form and thus binding to the -COOH functionalized SAM through hydrogen bonding, whereas on the -CO<sub>2</sub><sup>t</sup>Bu functionalized surface it cannot hydrogen bond. The preference for NR<sub>2</sub>-PL to bind at pH 3 over pH 9 could also be explained by referring to the  $pK_a$ values of the substrate and the particles. The monolayer as described earlier will be nearly fully deprotonated at pH 9. The



Fig. 9 Tapping mode AFM topography images of the SAMs after immersion in aqueous solution of  $NR_2$ -PL nanoparticles: (a) on the **MHBTE (I)** SAM at pH 3, (b) on the **MHBTE (I)** SAM at pH 9, (c) on the **MHBA (III)** SAM at pH 3 and (d) on the **MHBA (III)** SAM at pH 9.

 $pK_a$  of tertiary amine is reported to be between 10.6–10.7 when in free solution.<sup>49,50</sup> However, the  $pK_a$  of primary amines at the periphery of SAMs has been reported as 6,<sup>51</sup> which is lower than the  $pK_a$  of primary amines in free solution. Thus, the  $pK_a$ of the NR<sub>2</sub>-PL nanoparticles could be lower than expected. Presuming the  $pK_a$  for the tertiary amine on the nanoparticles is between 6–10, most of the particles are not protonated, and therefore there is no complementary interaction between the SAM and the NR<sub>2</sub>-PL nanoparticles.

2.6.3 Summary of the attachment of nanoparticles on the SAMs. Both COOH-PL and NR<sub>2</sub>-PL nanoparticles exhibit stronger affinities for the –COOH functionalized monolayer compared to the  $-CO_2^{t}$ Bu functionalized monolayer at pH 3. At pH 9, there are virtually no particles attached to either surface. In addition, it has been shown that the NR<sub>2</sub>-PL nanoparticles have a stronger affinity for the –COOH functionalized monolayer at pH 3 in comparison with COOH-PL nanoparticles, which is reflected in the particle densities on the respective substrates which are observed as 104 and 29 particles  $\mu m^{-2}$ , respectively.

2.6.4 NR<sub>2</sub>-PL attachment onto the acid gradient SAM. After the gradient hydrolysis of the MHBTE (I) SAM using the Peltier element, the substrate was immediately immersed into NR<sub>2</sub>-PL solution at pH 3 for 2 h, followed by rinsing with UHQ H<sub>2</sub>O, dried with a stream of N<sub>2</sub> and stored in sealed sample holders until the samples were analysed. NR<sub>2</sub>-PL nanoparticles were chosen as these particles had the largest difference in particle attachment between the -COOH and -CO<sub>2</sub><sup>t</sup>Bu functionalized surfaces. AFM images taken along the substrate were taken within 24 h of being removed from the particle solution to minimise contaminants adsorbing on the surfaces. From the images (Fig. 10a) it is evident that the particle density along the substrate gradually decreases to zero. Fig. 10b depicts the average particle density along the substrate determined from the AFM images. The particle density decreases exponentially from 64 particles  $\mu m^{-2}$  at 0 mm to 0 particles  $\mu m^{-2}$  at 12 mm from the setpoint, and this correlates with the fractional surface coverage of -COOH moieties on the underlying SAM.

#### **3** Experimental

#### 3.1 Chemicals

Commercially available chemicals were purchased from Aldrich, Acros or Lancaster and used as received. The functionalized polystyrene nanoparticles were purchased from Bangs Labs, USA. The different pH solutions were prepared either by the addition of HCl (0.5 M) to obtain the aqueous solutions with pH in the range 1–5 or by the addition of NaOH (0.5 M) to obtain aqueous solutions with pH in the range 6–13 to UHQ H<sub>2</sub>O. pH was measured using a thin stem stainless pH reference probe (ISFET electrode), which was two point calibrated with phosphate buffers. For measuring aqueous solutions in the pH range 1–7, phosphate buffers pH 4.0 and 7.0 were used for the two point calibration of the pH probe and for measuring the higher pHs (8–13), phosphate buffers pH 7.0 and pH 9.18 were used. Thin-layer chromatography



Fig. 10 (a) Tapping mode AFM topography images taken along the modified substrate after being immersed in colloidal solution of  $NR_2$ -PL solution at pH 3 and (b) the average particle density along the acid gradient substrate determined from the AFM images.

(TLC) was carried out on aluminium plates coated with silica gel 60 F254 (Merck 5554). For the aryl-based compounds the TLC plates were air-dried and analysed under a short wave UV lamp (254 nm), whereas for the aliphatic compound the TLC plates were air dried and developed in an  $I_2$  chamber. Column chromatographic separations were performed on silica gel 120 (ICN Chrom 32–63, 60 Å).

#### 3.2 Synthesis of the aryl-based thiols

4-Hydroxybenzoic acid *tert*-butyl ester (2a). To a solution of 4-hydroxybenzoic acid (1) (5.00 g, 36.22 mmol), 4-DMAP (0.17 g, 1.40 mmol) and *tert*-butanol (100 ml) in dry THF (150 ml) under N<sub>2</sub> atmosphere, a solution of DCC in dry THF (50 ml) was added dropwise at room temperature for 30 min. The reaction mixture was stirred at room temperature under N<sub>2</sub> atmosphere for 20 h. The residue mixture was filtered and the filtrate was concentrated *in vacuo* (~20 ml). The filtrate was washed with 0.3 M Na<sub>2</sub>CO<sub>3</sub> solution (3 × 40 ml), dried (MgSO<sub>4</sub>), filtered and concentrated *in vacuo*. The pale yellow crude product was purified by flash silica gel chromatography (graded elution: 0 to 30% EtOAc in hexane, increase polarity in increments of 5% per 100 ml of eluent used). The solvent was removed *in vacuo* to yield a white solid (6.68 g, 95%). Mp: 118–120 °C;  $v_{max}/cm^{-1}$  (Nujol): 3302 (OH), 2923 (CH), 2854 (CH), 1678 (C=O), 1608 (benzene ring), 1590 (benzene ring);  $\delta_{\rm H}(300 \text{ MHz}; \text{CDCl}_3; \text{Me}_4\text{Si})$  7.89 (2 H, d, J = 8.64 Hz, ArH), 6.85 (2 H, d, J = 8.64 Hz, ArH), 6.18 (1 H, br s, Ar*OH*), 1.58 (9 H, s, C(*CH*<sub>3</sub>)<sub>3</sub>);  $\delta_{\rm C}(75 \text{ MHz}; \text{CDCl}_3; \text{Me}_4\text{Si})$  169.0, 161.8, 133.4, 125.2, 116.9, 83.1, 30.0; m/z (ESMS): 217 ([M + Na]<sup>+</sup>, 100%); HRMS: found 217.0846; calc. mass for C<sub>11</sub>H<sub>14</sub>O<sub>3</sub>Na: 217.0841.

**4-Hydroxybenzoic acid methyl ester (2b).** A solution of 4-hydroxybenzoic acid (1) (5.00 g, 36.22 mmol) and conc. H<sub>2</sub>SO<sub>4</sub> (0.5 ml) in MeOH (100 ml) was heated under reflux for 20 h. The reaction mixture was allowed to cool to room temperature and concentrated *in vacuo* (20 ml). Water (100 ml) was added and the aqueous layer was extracted with Et<sub>2</sub>O (3 × 75 ml). The combined organic layers were washed with brine (50 ml), dried (MgSO<sub>4</sub>) and filtered. The solvent was removed *in vacuo* to afford a white solid (5.08 g, 92%). Mp: 118–120 °C;  $v_{max}/cm^{-1}$  (Nujol): 3281 (OH), 2926 (CH), 2854 (CH), 1681 (C=O), 1608 (benzene ring), 1587 (benzene ring);  $\delta_{\rm H}(300 \text{ MHz}; \text{ CD}_3\text{OD}; \text{ Me}_4\text{Si})$  7.89 (2 H, d, J = 8.64 Hz, ArH), 6.84 (2 H, d, J = 8.64 Hz, ArH), 3.84 (3 H, s, OCH<sub>3</sub>);  $\delta_{\rm C}(75 \text{ MHz}; \text{CD}_3\text{OD}; \text{Me}_4\text{Si})$  169.0, 163.1, 133.3, 123.1, 116.7, 52.8; *mlz* (ESMS): 175 ([M + Na]<sup>+</sup>, 100%).

1-(6-Bromohexyloxy)benzoic acid tert-butyl ester (3a). A suspension of K<sub>2</sub>CO<sub>3</sub> (5.45 g, 39.49 mmol) in a solution of 2a (3.83 g, 19.74 mmol), 1,6-dibromohexane (9.63 g, 39.47 mmol) in MeCN (150 ml) was heated under reflux with a CaCl<sub>2</sub> guard for 20 h. The reaction mixture was allowed to cool to room temperature and concentrated in vacuo (20 ml). Water (100 ml) was added and the aqueous layer was extracted by washing with EtOAc (3  $\times$  50 ml). The combined organic layers were washed with brine (20 ml), dried (MgSO<sub>4</sub>), filtered and solvent removed in vacuo, yielding a white solid as the crude product. The solid was absorbed onto silica and purified via silica gel column chromatography (graded elution: 0 to 30% EtOAc in hexane, increase polarity in increments of 5% per 100 ml of eluent used). The solvent was removed in vacuo to yield a white solid (5.36 g, 76%). Mp: 45–46 °C; v<sub>max</sub>/cm<sup>-1</sup> (film): 2924 (CH), 2854 (CH), 1702 (C=O), 1605 (benzene ring), 1511 (benzene ring);  $\delta_{\rm H}(300 \text{ MHz}; \text{CDCl}_3; \text{Me}_4\text{Si})$  7.91 (2 H, d, J = 8.82 Hz, ArH), 6.86 (2 H, d, J = 8.82 Hz, ArH), 3.99 (2 H, t, J = 6.25 Hz,  $OCH_2C_5H_{10}Br$ ), 3.41 (2 H, t, J = 6.44 Hz, OC<sub>5</sub>H<sub>10</sub>CH<sub>2</sub>Br), 1.90–1.78 (4 H, m, OCH<sub>2</sub>CH<sub>2</sub>C<sub>2</sub>H<sub>4</sub>CH<sub>2</sub>-CH<sub>2</sub>Br), 1.58 (9 H, s, C(CH<sub>3</sub>)<sub>3</sub>), 1.54–1.50 (4 H, m,  $OC_2H_4C_2H_4C_2H_4Br$ );  $\delta_C(75 \text{ MHz}; \text{ CDCl}_3; \text{ Me}_4\text{Si})$  167.7, 164.4, 133.9, 126.5, 116.4, 83.0, 70.4, 36.3, 35.2, 31.5, 30.8, 30.4, 27.8; *m*/*z* (EIMS): 379 ([M]<sup>+</sup>, 100%), 381 ([M<sup>+</sup>], 80%); HRMS: found 379.0892; calc. mass for C<sub>17</sub>H<sub>25</sub>O<sub>3</sub>BrNa: 379.0885.

4-(6-Bromohexyloxy)benzoic acid methyl ester (3b). The procedure described for the synthesis of compound 3a was followed, however using compound 2b (3.00 g, 19.74 mmol), 1,6-dibromohexane (9.63 g, 39.47 mmol) and  $K_2 CO_3$  (5.45g, 39.49 mmol) in MeCN (150 ml). This afforded a white solid (4.76 g, 77%). Mp: 50–51 °C; v<sub>max</sub>/cm<sup>-1</sup> (Nujol): 2925 (CH), 2858 (CH), 1723 (C=O), 1608 (benzene ring), 1510 (benzene ring);  $\delta_{\rm H}(300 \text{ MHz}; \text{CDCl}_3; \text{Me}_4\text{Si})$  7.97 (2 H, d, J = 8.64 Hz,Ar*H*), 6.89 (2 H, d, *J* = 8.64 Hz, Ar*H*), 4.00 (2 H, t, *J* = 6.44 Hz,  $OCH_2C_5H_{10}Br$ ), 3.87 (3 H, s,  $OCH_3$ ), 3.42 (2 H, t, J = 6.78 Hz,  $OC_5H_{10}CH_2Br$ ), 1.91–1.79 (4 H, m,  $OCH_2CH_2C_2H_4$ - $CH_2CH_2Br$ ), 1.52–1.49 (4 H, m,  $OC_2H_4C_2H_4C_2H_4Br$ );  $\delta_{\rm C}$ (75 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si) 167.0, 162.6, 132.6, 123.2, 115.0, 68.9, 52.8, 34.7, 33.6, 29.9, 28.9, 26.2; m/z (ESMS): 339 ([M + Na]<sup>+</sup>, 97%), 337 ([M + Na]<sup>+</sup>, 100%); *m/z* HRMS: found 377.0430; calc. mass for  $C_{14}H_{19}O_3$ NaBr: 337.0415.

4-(6-Mercaptohexyloxy)benzoic acid *tert*-butyl ester (MHBTE (I)). A solution of 3a (1.13 g, 3.18 mmol) and thiourea (0.27 g, 3.50 mmol) in anhydrous EtOH (40 ml) was heated under reflux and N<sub>2</sub> atmosphere for 20 h. 5 M aqueous NaOH (0.64 ml, 3.18 mmol) was added and the reaction mixture further heated under reflux for 20 h. The mixture was allowed to cool to room temperature and concentrated *in vacuo* (20 ml). Water (50 ml) was added and acidified with 2 M HCl to yield a white precipitate. The white precipitate was dissolved by CH<sub>2</sub>Cl<sub>2</sub> (50 ml) and the aqueous layer extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 × 50 ml). The combined organic layers were dried (MgSO<sub>4</sub>), filtered and solvent removed *in vacuo* to yield a white solid as the crude product. The solid was absorbed onto silica and purified *via* silica gel column chromatography (graded elution: 0 to 25% EtOAc in hexane, increase polarity in increments of 5% per 100 ml of eluent used). This afforded a white solid (0.72 g, 78%). Mp: 42–43 °C; elemental analysis found: C, 65.82%; H, 8.55%. Calc. for  $C_{17}H_{26}O_3S$ : C, 65.77%; H, 8.44%;  $v_{max}/cm^{-1}$  (film): 2925 (CH), 2854 (CH), 1705 (C=O), 1606 (benzene ring), 1512 (benzene ring);  $\delta_H(300 \text{ MHz}; \text{CDCl}_3; \text{ Me}_4\text{Si})$  7.91 (2 H, d, J = 8.83 Hz, ArH), 6.86 (2 H, d, J = 8.83 Hz, ArH), 3.99 (2 H, t,  $J = 6.44 \text{ Hz}, \text{O}CH_2\text{C}_5\text{H}_{10}\text{SH}$ ), 2.54 (q,  $J = 7.72 \text{ Hz}, 2\text{H}, \text{OC}_5\text{H}_{10}\text{C}H_2\text{SH}$ ), 1.81–1.77 (2 H, m, OCH<sub>2</sub>CH<sub>2</sub>C4H<sub>8</sub>SH), 1.67–1.60 (2 H, m, OC<sub>4</sub>H<sub>8</sub>CH<sub>2</sub>CH<sub>2</sub>SH), 1.57 (9 H, s, C(CH<sub>3</sub>)\_3), 1.48–1.45 (4 H, m, OC<sub>2</sub>H<sub>4</sub>C<sub>2</sub>H<sub>4</sub>-SH), 1.34 (1 H, t, J = 7.43 Hz, SH);  $\delta_C(75 \text{ MHz}, \text{CDCl}_3; \text{Me}_4\text{Si}$ ) 163.9, 160.0, 129.5, 122.5, 112.0, 78.6, 66.1, 32.0, 27.1, 26.4, 26.2, 23.6, 22.6; m/z (ESMS): 333 ([M + Na]<sup>+</sup>, 100%); m/z (HRMS): found 310.1612; calc. mass for  $C_{17}H_{26}O_3$ S: 310.1609.

4-(6-Mercaptohexyloxy)benzoic acid methyl ester (MHBME (II)). The procedure described for the synthesis of compound MHBTE (I) was followed, however using compound 3b (1.00 g, 3.18 mmol), thiourea (0.27 g, 3.55 mmol) and 5 M NaOH (0.64 ml, 3.18 mmol) in EtOH (40 ml). This afforded a white solid (0.61 g, 73%). Mp: 45-46 °C; elemental analysis found: C, 62.64%; H, 7.50%. Calc. for C14H20O3S: C, 62.66%; H, 7.51%; v<sub>max</sub>/cm<sup>-1</sup> (Nujol): 2922 (CH), 2854 (CH), 1724 (C=O), 1608 (benzene ring), 1510 (benzene ring);  $\delta_{\rm H}(300 \text{ MHz}; \text{ CDCl}_3;$ Me<sub>4</sub>Si) 8.19 (2 H, d, J = 9.20 Hz, ArH), 6.93 (2 H, d, J =9.20 Hz, ArH), 4.04 (2 H, t, J = 6.44 Hz, OCH<sub>2</sub>C<sub>5</sub>H<sub>10</sub>SH), 3.87 (3 H, s,  $OCH_3$ ), 2.54 (2 H, q, J = 7.72 Hz, OC<sub>5</sub>H<sub>10</sub>CH<sub>2</sub>SH), 1.85–1.80 (2 H, m, OCH<sub>2</sub>CH<sub>2</sub>C<sub>4</sub>H<sub>8</sub>SH), 1.67-1.63 (2 H, m, OC<sub>4</sub>H<sub>8</sub>CH<sub>2</sub>CH<sub>2</sub>SH), 1.49-1.47 (4 H, m,  $OC_2H_4C_2H_4C_2H_4SH$ , 1.34 (1 H, t, J = 7.72 Hz, SH);  $\delta_{\rm C}$ (75 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si) 166.0, 161.7, 130.4, 121.2, 112.9, 66.8, 50.6, 32.7, 27.8, 26.9, 24.3, 23.3; m/z (ESMS): 291 ([M +  $Na_{1}^{+}$ , 100%); *m/z* (HRMS): found 291.1027; calc. mass for C<sub>14</sub>H<sub>20</sub>O<sub>3</sub>SNa: 291.1031.

4-(6-Mercaptohexyloxy)benzoic acid (MHBA (III)). The procedure described for the synthesis of compound MHBTE (I) was followed, using compound 3b (1.00 g, 3.18 mmol), thiourea (0.27 g, 3.55 mmol) and 5 M NaOH (1.54 ml, 9.54 mmol) in EtOH (40 ml). This afforded a white solid (0.59 g, 73%). Mp: 112-114 °C; elemental analysis found: C, 61.51%; H, 6.93%. Calc. for C<sub>13</sub>H<sub>18</sub>O<sub>3</sub>S: C, 61.39%; H, 7.13%; v<sub>max</sub>/cm<sup>-1</sup> (Nujol): 2924 (CH), 2853 (CH), 1674 (C=O), 1607 (benzene ring), 1514 (benzene ring);  $\delta_{\rm H}(300 \text{ MHz}; \text{ CDCl}_3:$ Me<sub>4</sub>Si) 8.04 (2 H, d, J = 8.64 Hz, ArH), 6.93 (2 H, d, J =8.64 Hz, ArH), 4.02 (2 H, t, J = 6.44 Hz, OCH<sub>2</sub>C<sub>5</sub>H<sub>10</sub>SH), 2.54  $(2 \text{ H}, \text{q}, J = 7.27 \text{ Hz}, \text{ OC}_5\text{H}_{10}CH_2\text{SH}), 1.84-1.79 (2 \text{ H}, \text{m}, 1.84-1.79)$ OCH<sub>2</sub>CH<sub>2</sub>C<sub>4</sub>H<sub>8</sub>SH), 1.67-1.63 (2 H, m, OC<sub>4</sub>H<sub>8</sub>CH<sub>2</sub>CH<sub>2</sub>SH), 1.48–1.45 (4 H, m,  $C_2H_4C_2H_4C_2H_4SH$ ), 1.34 (1 H, t, SH);  $\delta_{\rm C}(75 \text{ MHz}; \text{CDCl}_3; \text{Me}_4\text{Si})$  166.8, 162.0, 131.1, 122.8, 114.0, 67.4, 33.1, 28.2, 27.2, 24.7, 23.5; *m/z* (EIMS): 254 ([M]<sup>+</sup>, 50%).

#### 3.3 Compound characterisation

**3.3.1 NMR.** <sup>1</sup>H Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker AC 300 (300.13 MHz) spectrometer. <sup>13</sup>C NMR spectra were recorded on a Bruker AV 300 (75.5 MHz) using Pendent pulse sequences. All chemical shifts are quoted in ppm to higher frequency from Me<sub>4</sub>Si using either

deuterated chloroform (CDCl<sub>3</sub>) or methanol (CD<sub>3</sub>OD) as the lock and the residual solvent as the internal standard. The coupling constants are expressed in hertz (Hz) with multiplicities abbreviated as follows: s = singlet, d = doublet, dd = doublet, t = triplet, q = quartet and m = multiplet.

**3.3.2 Mass spectrometry (MS).** Electron impact mass spectroscopy (EIMS) was performed on a VG Prospec. Low and high resolution electrospray mass spectrometry was performed on a Micromass time of flight (TOF) instrument using methanol as the mobile phase.

**3.3.3 Infrared spectroscopy (IR).** The IR spectra were recorded as thin solid films on NaCl discs using a Perkin Elmer 1600 FT-IR. The solids were mixed with Nujol to form a paste which was spread between the NaCl discs to form a thin film.

**3.3.4 Elemental analysis.** Elemental analyses were carried out on a Carlo Erba EA 1110 (C H N) instrument.

#### 3.4 Preparation of Au substrates

The gold substrates were prepared using an Auto 306 vacuum evaporation chamber (Edwards) in a two pump system, the pressure was reduced to  $\sim 10^{-4}$  bar followed by a subsequent reduction to  $\sim 10^{-7}$  bar. Gold was deposited onto glass microscope slides (BDH). Prior to the evaporation of gold onto the glass slides, a Cr layer (6 nm) was evaporated onto the glass slides by heating Cr pieces (Agar Scientific, 99.99% purity) of  $\sim 5 \text{ mm}^3$  volume by electrical resistance using a voltage of 30 V and a current of 3 A, to promote adhesion of the gold to the base material. Au was deposited in a similar manner, with Au wire (Advent Research Materials, 99.99+% purity) of 0.5 mm diameter, which was placed into a Mo boat (Agar Scientific) and heated. The Au wire was heated by electrical resistance using a voltage of 10 V and a current of 3 A until  $\sim 100$  nm of Au had been deposited onto the desired surface within the auto 306 vacuum evaporation chamber. Deposition and deposition rate were monitored using a quartz crystal microbalance (QCM) thickness monitor. A deposition rate between 0.05–0.1 nm  $s^{-1}$  was used for both Cr and Au layers. The Au substrates were cut up into smaller pieces (1  $\times$  $1 \text{ cm}^2$ ) for the preparation of samples for characterisation and  $(2.5 \times 2.5 \text{ cm}^2)$  for the preparation of the acid gradient SAMs prior to use, using a diamond tipped scriber.

#### 3.5 Preparation of SAMs

Prior to the preparation of the SAMs the glassware and the gold substrates were cleaned thoroughly to remove contaminants. Initially, the glassware was washed thoroughly with piranha solution (conc.  $H_2SO_4$ : 30%  $H_2O_2 = 7:3$ ) followed by rinsing with UHQ  $H_2O$ . The subsequent steps were followed: sonication in UHQ  $H_2O$  for 30 min, drying in an oven at 120 °C for 30 min, allowed to cool to room temperature, sonication in EtOH for 30 min, drying in an oven at 120 °C for 30 min and wrapping in aluminium foil before use to prevent exposure to airborne contaminants and use within 24 h. The Au substrates were immersed in piranha solution at room

temperature for 10 min with occasional stirring, followed by thorough rinsing with UHQ H<sub>2</sub>O, then with EtOH (HPLC grade) and immediately immersed in the desired 1 mM solution of **MHBTE** (I), **MHBME** (II) and **MHBA** (III) for 24 h. Finally, the SAMs were rinsed thoroughly with EtOH (HPLC grade) and dried with a stream of N<sub>2</sub>.

#### 3.6 SAM characterisation

3.6.1 Water contact measurements. Contact angles were determined using a home-built contact angle apparatus, equipped with a charged coupled device (CCD) KP-M1E/K camera (Hitachi) that was attached to a personal computer for video capture. FTÅ Video Analysis software v1.96 (First Ten Angstroms) was used for the analysis of the contact angle of a droplet of UHQ H<sub>2</sub>O at the three-phase intersection. The dynamic contact angles were recorded as a micro-syringe was used to quasi-statically add liquid to or remove liquid from the drop. The drop was shown as a live video image on the PC screen and digitally recorded for future analysis. The acquisition rate was 4 frames per second. The static contact angles were measured by placing a  $H_2O$  (UHQ) droplet (1  $\mu$ L) on the substrate and the images were recorded digitally in the same way as the dynamic contact angles. The contact angles were determined from an average of fifteen different measurements made on each type of SAM. Three samples were prepared for each SAM and five measurements were taken from different areas on each sample, except for the contact angles measured on the acid gradient SAMs where three contact angles were taken for each position along each of the three acid gradient SAMs prepared. The errors reported for the contact angle measurements are standard errors.

**3.6.2 Ellipsometry.** The thickness of the deposited monolayers was determined by spectroscopic ellipsometry. A Jobin-Yvon UVISEL ellipsometer with a xenon light source was used for the measurements. The angle of incidence was fixed at 70°. A wavelength range of 280–820 nm was used. The DeltaPsi software was employed to determine the thickness values and the calculations were based on a three-phase ambient/SAM/Au model, in which the SAM was assumed to be isotropic and assigned a refractive index of 1.50. The thickness reported is the average of six measurements taken on each SAM.

3.6.3 X-Ray photoelectron spectroscopy (XPS). Elemental composition of the SAMs were analysed using an Escalab 250 system (Thermo VG Scientific) operating with Avantage v1.85 software under a pressure of ~5 × 10<sup>-9</sup> mbar. An Al K<sub>α</sub> X-ray source was used, which provided a monochromatic X-ray beam with incident energy of 1486.68 eV and a circular spot size of ~0.2 mm<sup>2</sup> was employed.

The samples were attached onto a stainless steel holder using double-sided carbon sticky tape (Shintron tape). In order to minimise charge retention on the sample, the samples were clipped onto the holder using stainless steel or Cu clips. The clips provided a link between the sample and the sample holder for electrons to flow, which the glass substrate inhibits.

Low resolution survey spectra were obtained using a pass energy of 150 eV over a binding energy range of -10 eV to

1200 eV obtained using 1 eV increments. The spectra recorded were an average of 3 scans. The high resolution spectra were obtained using a pass energy of 20 eV and 0.1 eV increments over a binding energy range of 20–30 eV, centred on the binding energy of the electron environment being studied. A dwell time of 20 ms was employed between each binding energy increment.

#### 3.7 Hydrolysis of MHBTE (I) and MHBME (II) SAMs

To avoid any unnecessary contamination, the freshly prepared SAMs were immersed immediately into the preheated aqueous acidic/basic solution (20 ml) at the required temperature for 5 h. After this duration, the substrates were rinsed with copious amounts of UHQ H<sub>2</sub>O and dried with a stream of N<sub>2</sub>. Contact angle measurements were taken immediately to avoid contamination of the surface, which may influence the data obtained.

#### 3.8 Temperature gradient on the MHBTE (I) SAM

The temperature gradient was obtained by mounting 5 mm of the Au substrate with MHBTE (I) SAM (dimensions 25 mm  $\times$ 20 mm) onto the Peltier element with the setpoint as shown in Fig. 5 being 3 mm from one of the edges. The temperature along the substrate was measured in air and determined using K-type thermocouples which were connected to a thermocouple module (iso-tech ITA11) and readings taken on a voltmeter (Caltek instrument, CM1200T). The current to the Peltier element was supplied by a Ranger power unit (0-13 V, 8 A). The Au substrate (dimensions  $25 \times 20$  mm) was mounted on the Peltier element (dimensions:  $30 \times 30$  mm) with Loctite glass bond glue. The Peltier element with the substrate was placed upon a metal block to act as a heat sink, so that the temperature gradient through the substrate remained stable. Three temperature readings were taken at each point along the Au substrate (0, 2, 4, 6, 8, 10, 12, 14, 16, 18 and 20 mm); the variation in the measurements across the substrate is shown by the standard error.

## 3.9 Preparation of the acid gradient substrate on the Peltier element

A Au substrate with dimensions  $25 \times 20$  mm was mounted onto a custom built rectangular shaped glass cell ( $25 \times 20 \text{ mm}$ ) with Loctite glass bond glue to form the reaction cell. 1 mM MHBTE (I) ethanolic solution (5 ml) was poured into the reaction cell and covered with aluminium foil for 24 h. After 24 h, the MHBTE (I) solution was removed and the reaction cell was rinsed thoroughly with copious amounts of HPLC EtOH followed by drying with N<sub>2</sub>. The reaction cell was immediately glued onto the Peltier element with Loctite glass bond glue and allowed to dry for 5 min, covered with aluminium foil to avoid contaminating the surface. The hot end of the cell (end mounted onto the Peltier element) was heated to 80 °C, followed by the addition of the aqueous pH 1 solution (0.5 ml). The temperature was maintained at 80 °C for the duration of the hydrolysis by monitoring the temperature at the exposed corners of the Au substrate. Also the volume of the aqueous solution was monitored. After the duration of the

heating, the aqueous solution was removed followed by the Au substrate being removed from the reaction cell and great care was taken to avoid damage to the substrate. The substrate was thoroughly rinsed with copious amount of UHQ  $H_2O$  and dried with a stream of  $N_2$ .

#### 3.10 Attachment of nanoparticles

**3.10.1 MHBTE (I) and MHBA (III) SAMs.** After their preparation, the SAMs were immersed in the colloidal solutions (5 mg ml<sup>-1</sup>, 2 ml) at either pH 3 or pH 9 for 2 h, followed by rinsing with copious amounts of UHQ H<sub>2</sub>O for 30 s and drying with a stream of N<sub>2</sub>. The average particle density was determined by counting the number of particles on three AFM images taken from each sample.

**3.10.2 Acid gradient substrate.** The modified surface was immersed immediately after being modified by the Peltier element in NR<sub>2</sub>-PL nanoparticle solution (5 mg ml<sup>-1</sup>) at pH 3 (25 ml) for 2 h, followed by rinsing with copious amounts of UHQ H<sub>2</sub>O for 1 min and drying with a stream of N<sub>2</sub>. The average particle density at each point along the substrate was determined from three AFM images taken across the substrate for each point.

#### 4 Conclusion

The work described has demonstrated that the confinement of the ester moieties at the terminus of quasi-crystalline SAMs limits the hydrolysis of the esters. Thus, -CO<sub>2</sub>Me moieties do not hydrolyse in either acidic or basic media and  $-CO_2^{t}Bu$ moieties do not hydrolyse in basic media. It is concluded that the lack of hydrolysis is due to the molecules being confined in closely packed monolayers, which does not allow the attacking nucleophilic water access to the electrophilic carbonyl carbon atom, *i.e.* the attack trajectory is sterically hindered. This steric argument is supported by considering the relative ease of the acid-catalysed hydrolysis of -CO<sub>2</sub><sup>t</sup>Bu moieties which proceeds via the AAL1 mechanism, whereby there is no requirement for attack by a nucleophile, only protonation of the carbonyl oxygen that leads to the release of a <sup>t</sup>Bu cation (which collapses to isobutene and a proton). Furthermore, detailed analysis of the activation energy of the SAM hydrolysis revealed that the  $pK_a$  of the ester functional group had a profound effect on the activation energy, further supporting the A<sub>AL</sub>1 mechanism in the case of the -CO<sub>2</sub><sup>t</sup>Bu SAM.<sup>15</sup> Thus, when designing SAMs on which surface chemistry is to be carried out it is important to pay attention to the mechanisms associated with the chemical modification to ensure there is adequate space around the target functional group for the transformation to occur.

Moreover, a novel facile approach for the fabrication of a nanoparticle gradient substrate has been successfully demonstrated by the thermochemical manipulation of a  $-CO_2^{t}Bu$  functionalized SAM. An acid gradient SAM moving from -COOH to  $-CO_2^{t}Bu$  moieties provided the ideal underlying SAM onto which NR<sub>2</sub>-PL nanoparticles were attached at pH 3. The particles were shown to attach preferably onto the -COOH moieties and not to the  $-CO_2^{t}Bu$  moieties, resulting in

particle density starting from 104 particles  $\mu m^{-2}$  on the hydrolysed acid end reducing to 0 particles  $\mu m^{-2}$  on the non-hydrolysed end. The extent of the particle gradient could potentially be tuned by varying the pH at which the acid gradient SAM is immersed in the particle solution, or by the extent of the acid gradient in the underlying SAM, which can be controlled by the temperature and pH of the aqueous solution.

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