

Maskless nanopatterning and formation of nanocorrals and switches, for haloalkanes at Si(111)-7 × 7

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Abstract

Labile self-assembled circular patterns of propyl bromide on Si(111)-7 × 7 at 50 K are shown to convert to corresponding stable circular patterns of atomic bromine through a maskless process of molecular scale imprinting. The imprinting depends on localized chemical reaction induced by either photons or electrons. At 50 K propyl bromide adsorbs in a vertical configuration with lateral attraction. By contrast, at 300 K, octyl chloride and bromide adsorbed horizontally, self-assembling spontaneously into the valuable configurations of switching corrals ('type I') and stable corrals ('type II'). Both types of corral, switching and stable, can be seen to alter the local surface charge distribution.

1. Introduction

Scanning tunnelling microscopy (STM) has proved to be the enabling tool of the nano-age, allowing the nanoengineer to see what has been constructed [1]. Previously inconceivable nanostructures have been made using the STM's ability to detect single atoms, as well as its ability to manipulate them to form engineered structures such as 'corrals' which constitute extended artificial atoms [2].

It is widely recognized, however, that the path to constructing nanodevices is through self-assembly of the desired nanopatterns [3–6] rather than through an-atom-at-a-time fabrication. At the same time it must be recognized that self-assembly demands mobility, whereas a useful nanostructure must be immobile even when subject to such common stresses as repeated electrical charging and discharging [7]. Section 3 of the present paper, entitled 'Localized reaction', gives new evidence for a method of nanopattern stabilization by photon- or electron-induced 'molecular scale imprinting' on the underlying surface [8–10].

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Section 4 reports further evidence for self-assembly of long chain haloalkanes on silicon forming robust corrals [11–13] and switches [14]. Section 5 presents new evidence as regards the mobile precursor state that gives haloalkanes (propyl bromide here) the ability to self-assemble into the types of pattern illustrated in the previous two sections, despite the roughness of Si(111)-7 × 7.

2. Experimental methods

Room temperature and low temperature topographic images were obtained using an RHK-400 scanning tunnelling microscope (STM) in the first instance and an Omicron VT-STM in the second. Both systems have been described previously [15, 16] and have a base pressure less than 10⁻¹⁰ Torr. Cooling was by liquid helium. STM tips were electrochemically etched from 0.25 mm polycrystalline tungsten wire in a 2.0 M NaOH solution. The STMs were operated in the constant-current mode at a tunnelling current of 0.2 nA.

Silicon (111) samples (2 × 9 mm²) were cut from n-type phosphorus-doped silicon wafers (250 ± 25 μm in thickness) with a resistivity of 0.02–0.05 Ω cm (Virginia

semiconductor). Samples were cleaned in UHV by several cycles of direct current heating to 1500 K for ~ 1 min. Temperatures were measured with an optical pyrometer (Minolta, $\epsilon = 0.63$) in the applicable temperature range. The STM images of the surface cleaned in this way showed a (7×7) reconstruction and a small number ($< 0.2\%$) of surface defects.

All reagents were from Aldrich, purified by freeze–pump–thaw cycles using liquid nitrogen, prior to introduction into the UHV chamber through a variable leak valve for background dosing. The composition of the dosant gases was checked using a residual gas analyser (SRS RGA-200). Exposures were measured in langmuirs ($1 \text{ L} = 1 \times 10^{-6} \text{ Torr s}$) with pressure measured at an uncorrected ion gauge calibrated for N_2 . Ion gauges have a high sensitivity to long chain alkane molecules [17], approximate ‘true’ pressures of haloalkanes are obtained by dividing the measured pressures by 10.

3. Localized reaction

We have previously proposed a method of ‘maskless patterning’ for the nanoregime in which regime it is impractical to construct masks, since this would require shaping the masks with a molecular level of precision. The solution to this problem, as is widely recognized, is to make the molecules the patterning agent employing molecular ‘self-assembly’ as the first step in nanopatterning. A second step will, however, in general be required, since a self-assembled pattern formed from mobile adsorbates is likely to deteriorate if used in a device, such as a nanocircuit that ‘shakes’ the pattern through the repeated arrival and departure of charges [7]. A method that holds promise of solving this difficulty is to stabilize the self-assembled pattern, once formed, by light, electrons or heat to convert weak physisorption bonds into strong chemical ones [8].

The method [8, 9, 15, 16, 18–21] employs self-assembly of adsorbates for (labile) pattern formation, followed at a second stage by induced localized atomic reaction (‘LAR’) to convert the labile pattern into a stable one. Stability is achieved by induced chemical ‘imprinting’, since chemical bonds are an order of magnitude stronger than physical ones.

Crucial to this imprinting process is the requirement that the physisorbed pattern remain over the same substrate atomic location following the strong energization, typically requiring electronvolts of energy, needed to take the system over the energy barrier to chemical reaction. In the process of reaction the prior weakly bound physisorbed adsorbate is pulled down strongly to form chemical bonds with the surface. If the self-assembled pattern is to survive unaltered, this major change of state must occur without concurrent lateral motion across the surface [8, 16, 18–20, 15, 21].

In this work we give a new example of LAR and patterned nanoimprinting that satisfies these stringent requirements. The self-assembled mobile adsorbate molecule, studied here by STM, we believe for the first time, is propyl bromide dosed typically for 100 s at an uncorrected pressure of 1.5×10^{-9} mbar. This adsorbate is shown in the STM image of figure 1(a) to spontaneously form molecular circles at a Si(111)- 7×7 surface in ultrahigh vacuum (UHV) at approximately 50 K. When irradiated with ultraviolet laser light pulses (6000 pulses at 1 mJ/pulse) at 193 nm (6.3 eV

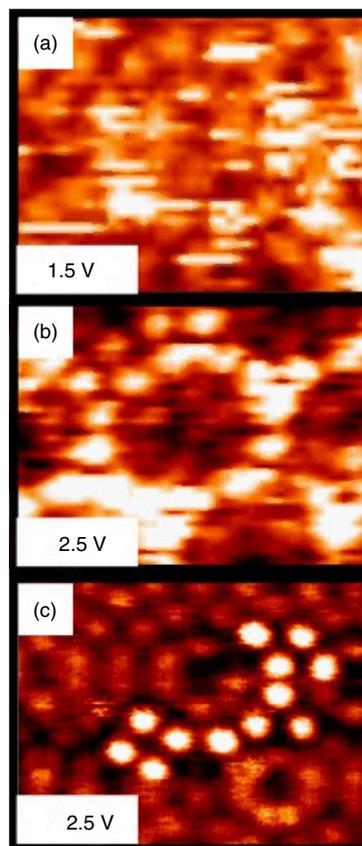


Figure 1. (a) A circle of physisorbed propyl bromide (which can be seen to be somewhat mobile under the tip, giving rise to streaks in scanning from left to right), (b) a circle of Br atoms photo-imprinted onto the Si(111)- 7×7 surface by ultraviolet light acting on physisorbed self-assembled circles of propyl bromide at 50 K (this circle is not the same one as shown in panel (a)), (c) a part circle of Br atoms electron imprinted by scanning at 2.5 V surface bias (the scanning process causes some diffusion of the physisorbed precursor, as is evident even in the lower voltage scan of (a)).

energy/photon), figure 1(b), or, alternatively, irradiated with electrons with energy in excess of the 2.1 eV threshold energy for reaction, figure 1(c), corresponding circles of strongly chemically bound bromine atoms are formed by LAR, as shown. (A similar result may perhaps be achieved by thermally activated reaction, not examined here.)

These chemically imprinted circles due to photon- or electron-induced reaction resemble the prior physisorbed circles, demonstrating the ‘maskless imprinting’ process dependent on LAR. The most surprising feature of this process may be its apparent insensitivity to the energy delivered to the labile physisorbed reagent molecules (2.2 eV for electron impact up to 6.3 eV for photon-initiated reaction). A simple charge-transfer model (to and from the adsorbate) that may explain this localization of reaction even for energetic reagents has previously been proposed [16].

From earlier work [11, 13, 16] we know that haloalkanes on this substrate diffuse and self-assemble while in a mobile vertical state with the halogen atom ‘down’ (the attachment energy has been calculated to be ≈ 0.4 eV; [16]). The attraction must be greatest at ‘middle’ adatoms, in order to result in the observed physisorbed circles of figure 1(a) [16].

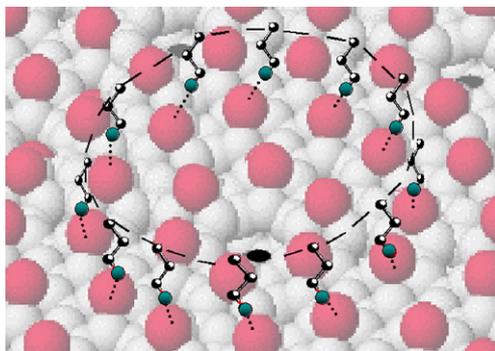


Figure 2. Scale model of propyl bromide physisorbed in circles on middle adatoms of Si(111)-7 × 7. Grey spheres represent silicon rest atoms and silicon atoms of lower layers, pink spheres are silicon adatoms, green spheres are bromine atoms, black spheres are carbon atoms; hydrogen atoms are not shown.

Irradiation with ultraviolet light or energetic electrons was found to cause either desorption or reaction. In the case of methyl bromide, desorption was approximately twice as probable as reaction [16]. In the present case of propyl bromide, the desorption probability was reduced by approximately an order of magnitude relative to the reaction probability, both for irradiation with 6.3 eV photons or 2.4 eV electrons. We attribute this to the stabilization of the adsorbate layer through adsorbate–adsorbate interaction in the case of the longer chain propyl bromide pictured in figure 2, as compared with methyl bromide (shown in its adsorbed state in [16]).

The type of adsorbate–adsorbate hydrocarbon chain interaction pictured in figure 2 is well known in self-assembled alkane thiols, adsorbed approximately vertically on gold [22]. It has not previously been reported for such short chains as the present three-carbon chain. Further, more direct evidence of this surprising ‘stacking’ of two- and three-carbon chains will be given in section 5.

In the following section we report new results for adsorbate–adsorbate interaction of haloalkanes in the horizontal state at room temperature (rather than the vertical state of 50 K, as above in figure 2). These further results are, once again at Si(111)-7 × 7. The horizontal adsorbates which will now be described self-assemble into corrals and switches (section 4).

4. Nanocorrals and switches

The previous section was concerned with intact haloalkanes adsorbed on Si(111) at low temperature (50 K) in a vertical state, with the halogen atom physisorbed at the surface. In this section we present results, once again obtained by STM, as regards the room temperature (300 K) physisorption of intact haloalkanes. Vertical adsorbates attached to single silicon atoms are no longer observed at room temperature, since they desorb. Instead the more strongly adsorbed horizontal molecules, spanning two or more adatom sites, are found. This is understandable since in addition to the heat of adsorption of the halogen atom (0.3–0.4 eV) the adsorbate gains an average of approximately 0.1 eV of adsorption energy for each CH₂ group of the alkane chain [23] (whether or not

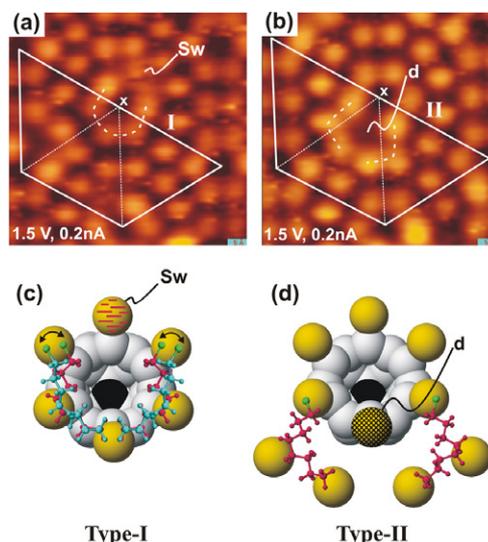


Figure 3. Self assembled molecular corrals formed by octyl bromide dimers. (a) High resolution STM image of a single type I corral (surrounding a corner hole) and (b) type II corral (surrounding a corner adatom). (c) and (d) are the space-filling models of type I and type II corrals respectively with ball-and-stick models of two 1-octyl bromide molecules, drawn to scale, superimposed; yellow spheres are silicon adatoms and the dark feature in the centre is the corner hole. Blue and red molecular configurations in (c) represent the on-state and off-state of the atom labelled ‘Sw’ respectively, and green denotes the bromine atom. ‘Sw’ is termed the switching adatom of the type I corral (streaked since it switches ‘on’ bright, and ‘off’, dark), ‘x’ is the corner hole and ‘d’ the darkened Si adatom of the type II corral. The double-headed arrow in (c) indicates that the halogenated ends of the pair of molecules constituting the type I corral are further from (‘on’) or closer to (‘off’) the adatom denoted ‘Sw’.

fully in register with an adatom below) for a total heat of adsorption in the region of 0.7 eV. This renders the horizontal monomeric and hence dimeric haloalkanes stable at the Si(111) surface [11–14].

Here we present recent results, not previously reported, on the adsorption and self-assembly of octyl halide, C₈H₁₇X, where X = Cl or Br. These long chain halides, in common with the 12-carbon dodecyl halides previously studied [11–14], appear in the STM topographs as horizontal monomers and dimers, in which each monomeric component covers 2–3 adatoms. Though the alkane chain is four carbon atoms shorter than in our earlier dodecane studies, the observed behaviour of the adsorbates is similar, serving to confirm the previous findings and indicate their generality.

In addition to the horizontal configuration, the most striking observation is the tendency of the adsorbate molecules to dimerize. Two types of dimer were observed, type I centred on a corner hole and type II on an adatom. Examples of each are shown for X = Br in figure 3. The case of X = Cl was found to be comparable to X = Br.

The most obvious feature of the dimers is their conformation as a curved pair, bracketing the atoms within. This has the appearance of a molecular corral [2]. In the previous study we demonstrated that there was indeed corralling of surface charge as evidenced by the darkened appearance of the corralled adatom. This corralling was further

characterized by scanning tunnelling spectroscopy (STS) and *ab initio* computation [11]. Darkening of a dangling bond in an ‘empty state’ image of the present type is characteristic of partial filling of that bond due to charge transfer inwards in the corral [11].

The darkening of the adatom at the centre of the type II corral is evident in the experimental STM topograph of figure 3 (shown for the case of the octyl bromide dimer). Here again, as for type I above, we have a corral that can be formed without the manual placing of atoms (cf [2]). Both of these types of self-assembled corral form on the technically interesting surface of silicon. The corrals are, in addition, stable at room temperature rather than only at the low temperature commonly employed to hold circles of mobile atoms in place. In our previous experiments the haloalkane corrals were stable to 100 °C [11].

The type I corrals, despite the altered chain length in the present work (eight carbons in place of the previous ten or twelve [14]), once again showed bistability, providing the basis for a molecular switch. This is evident in the dark streak in the STM image (figure 3(a)) of the silicon atom ‘Sw’ imprisoned between the jaws of the corral. The dark streak is indicative of a temporary change in electronic state of the corralled atom from conducting to non-conducting, and back, during the time of the trace over the single atomic site. *Ab initio* calculations reported previously correlated the conducting state with the configuration of the corral that opens the jaws and the non-conducting state with the configuration that closes the jaws of the corral around the imprisoned atom.

In our earlier work with a 12-carbon alkane chain we found that this thermally actuated switch involved up to an order-of-magnitude change in tunnelling current [14]. Switching occurred with a characteristic time in the region of a ms, comparable to the present case. Theory showed that small changes in the bistable corral configuration resulted in a shift in electronic energy of the corralled atom by of the order of 1 eV [14]. The off/on switching was attributed to increase/decrease in the surface dipole adjacent to the corralled Si adatom, due to in/out movement of the carbon–halogen bond at the halogenated ‘head’ of the switchable corral.

It has previously been suggested that self-assembly, particularly of large molecules, would not be observed at the naturally ‘rough’ surface of Si, involving dangling bonds at various elevations [24]. We have now demonstrated corral formation for alkane chain lengths of 8, 9, 12 and 18 carbons (no corrals were formed at room temperature for chains of 5 or 6 carbons) [11–14]. The observed stability of the corrals on silicon makes it even more surprising that they are able to self-assemble. This puzzle is solved if we invoke the long-lived vertical state of the haloalkane (noted at 50 K, previous section) as constituting a short-lived precursor state at 300 K, *en route* to the observed horizontal adsorbate [11, 13]. A further example of the vertical state at 50 K is given for two- and three-carbon chains in the following section.

5. Haloalkane diffusion on Si(111)-7 × 7

In this section we report, for two new cases, the distinctive mechanism for self-assembly by vertical molecules that glide across the surface loosely attached at a single halogen atom,

and thereafter lie down so as to contact the surface at multiple points and become immobilized. The most facile glide path across the surface appears to be the dimer row on Si(111), joining corner holes. The vertical molecules are like upright skiers on the piste, whereas the horizontal ones have become immobilized as is the case for fallen skiers.

At low temperature, as we have illustrated previously for 12-carbon-chain haloalkanes, we have now been able to observe vertical molecules (the ‘skiers’ in the analogy above) progressing along dimer rows for two- and three-carbon alkyl bromides [11–13]. The existence of these lines of skiers, rather than isolated molecules, even at low coverage is evidence of their affinity for one another even in the present examples of two- and three-carbon chains. We attribute this, most probably, to hydrogen bonding entanglement between even these short adjacent hydrocarbon tails when adjacent.

This has already been indicated in the visualization of the rings of propyl bromide adsorbate in figure 2 above, the evidence being the markedly reduced probability found (in the present work) for induced desorption of the individual molecules when irradiated with light or electrons, as compared with the earlier study of methyl bromide that lacked a hydrocarbon tail.

Significantly we have been unable to observe rows of methyl bromide ‘skiers’ lining up on our 50 K silicon surface. The presence of even a two- or three-carbon chain, we show in the present study, appears to be enough to give rise to the adsorbate–adsorbate attraction necessary for the (occasional) formation of such lines of ethyl bromide or propyl bromide, though not for methyl bromide. This is exemplified here in figure 4 for propyl bromide at 50 K. Similar topographs have been obtained for ethyl bromide at 50 K.

With this vertical precursor state confirmed by the observation of physisorbed rows of adsorbate at individual Si atoms, and by analogy with our earlier kinetic study of dodecyl halide [13], we propose a simple mechanism for the formation of dimeric corrals of the octyl chloride and octyl bromide of this study. The principal mechanism for corral formation proposed, as in the visualization of figure 5, involves a deceleration of motion of the vertical, *v*, molecules in their vertical encounters with corner holes, followed by attractive hydrogen bond interaction between pairs of alkane chains as for the nested lines of vertical molecules at low temperature shown in figure 4.

At room temperature a loosely bound molecular pair after leaving the dimer row topples into the observed horizontal dimeric configurations; type I if they fall in one direction around a corner hole, and type II if they fall in the other direction around an adatom.

Earlier work [11–13] showed evidence of a significant gain in stability for the horizontal pair (h_2) as compared with a horizontal monomer (*h*). This was evidenced by the fact that if one half of h_2 was removed from the surface, even at room temperature, by breaking its C–X bond by electron impact, the other half of the dimer desorbed. The dimer h_2 at the surface is stabilized relative to monomer by the observed charge transfer to its centre. The importance of this is highlighted by recent experiments in this laboratory that have shown that interference with this charge-transfer process by co-adsorption of a sub-monolayer of sodium causes all h_2 to separate into 2*h*.

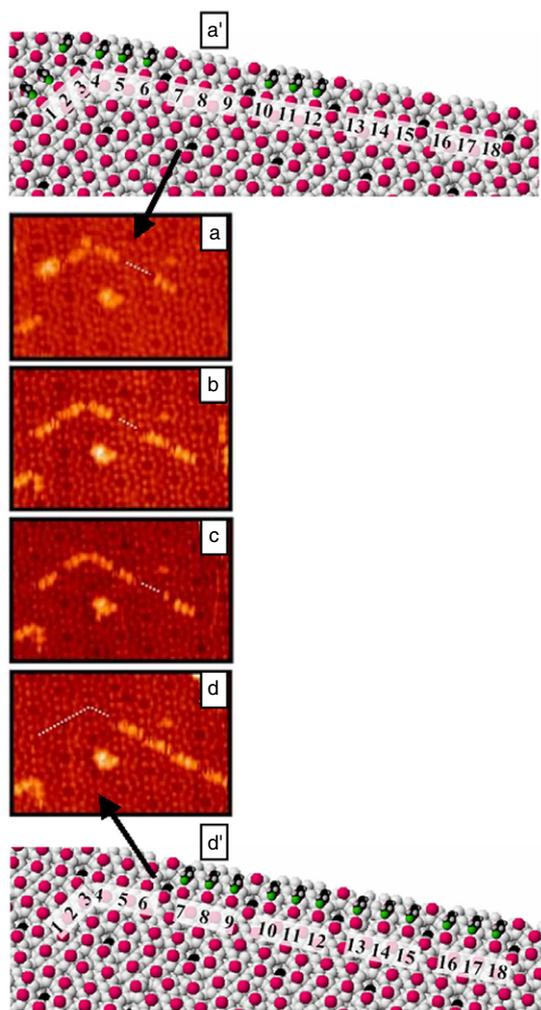


Figure 4. ((a)–(d)) Consecutive STM images of the same area of surface taken at intervals of approximately 40 s, showing physisorbed *n*-propyl bromide on Si dimer rows at 50 K, $I_{\text{tunn}} = 0.2$ nA, $V_s = 1.5$ V. The dimer rows link corner holes on Si(111)-7 × 7. Panels (a') and (d') give molecular models showing the approximate vertical arrangement of physisorbed propyl bromide molecules corresponding to the images recorded in (a) and (d) respectively (black = C, white = H, and green = Br in contact with the surface).

6. Conclusions

This paper presents new UHV-STM results as follows. Section 3 molecular scale pattern imprinting of strongly chemically bound bromine atoms at Si(111)-7 × 7 following photo-irradiation or electron irradiation of a self-assembled loosely physisorbed pattern of propyl bromide ($\text{C}_3\text{H}_7\text{Br}$) at 50 K, section 4 formation of stable corrals and also spontaneously switching corrals by the self-assembly of octyl halide ($\text{C}_8\text{H}_{17}\text{X}$) on Si(111)-7 × 7 at room temperature, and section 5 the mechanisms for haloalkane (specifically ethyl and propyl bromide) diffusion at 50 K across Si(111)-7 × 7 by movement as loosely bound vertical molecules along the dimer rows joining corner holes of the surface, with, at 300 K the vertical-to-horizontal transition, $2v \rightarrow h_2$, to yield the monomeric and dimeric (corral) horizontal structures of section 4.

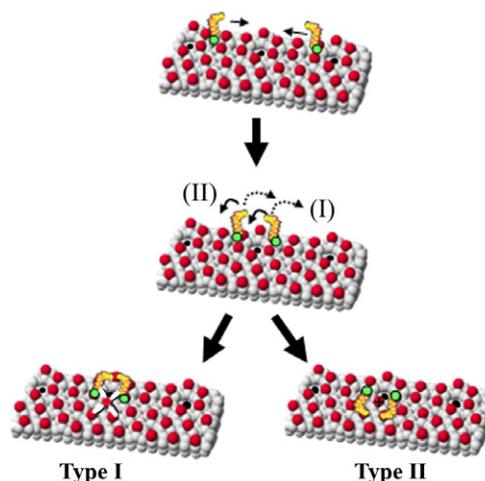


Figure 5. Schematic diagram showing corral formation at the Si(111)-7 × 7 surface. Two mobile physisorbed vertical monomers proceeding along dimer rows meet at a corner hole. Following migration to an adjacent corner adatom they ‘fall’ ($2v \rightarrow h_2$) to form either a type I or type II corral (around a corner hole or adjacent to a corner hole). For type I the corralled atom switched on and off (white rays) as the corral opens and closes. For type II the corralled atom (cross-hatched) is permanently dimmed.

The technical significance of section 3 is that it suggests a general means for mask-free imprinting of two-dimensional self-assembled nanostructures as stable patterns, by means of highly localized chemical reaction. The same localized molecular imprinting should be of value in ‘soldering’ nanostructures at selected points to the underlying surface, through the agency of the generalized application of light, electrons or heat resulting in the severance of weak C–X (here, carbon–halogen) bonds and local attachment (‘soldering’) to the surface at the same carbon atom through C–S covalent bonding (S symbolizes here an adjacent surface atom–silicon in the present instance).

The need for chemically localized soldering is evident from studies that show a $\times 10^4$ increase in electrical conductivity to the surface when a chemical bond is formed [25]. The attraction of the present method of photon and electron imprinting is that the sites at which atomically localized soldering attachment occurs can be specified through the molecular structure of the prior self-assembled substrate. There is no need to apply serially a nanoscale ‘soldering iron’ to the individual sites to be soldered, since the generalized application of energy (light, electrons or heat) results in concurrent localized reaction at all the desired sites of attachment.

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