

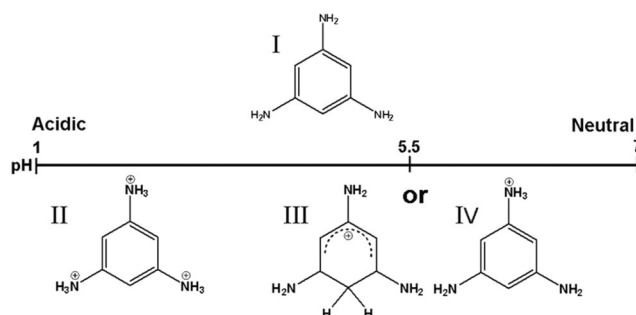
Amine-Directed Hydrogen-Bonded Two-Dimensional Supramolecular Structures

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Utilizing pure amine hydrogen bonding is a novel approach for constructing two-dimensional (2D) networks. Further, such systems are capable of undergoing structural modifications due to changes in pH. In this study, we designed a 2D network of triaminobenzene (TAB) molecules that by varying the pH from neutral to acidic, form either ordered or disordered structures on Au(111) surface as revealed in scanning tunneling microscopy images. In near-neutral solution (pH \approx 5.5), protonation of TAB generates charged species capable of forming H-bonds between amine groups of neighboring molecules resulting in the formation of a 2D supramolecular structure on the electrified surface. At lower pH, due to the protonation of the amine groups, intermolecular hydrogen bonding is no longer possible and no ordered structure is observed on the surface. This opens the possibility to employ pH as a chemical trigger to induce a phase transition in the 2D molecular network of triaminobenzene molecules.

Engineering well-ordered two-dimensional (2D) molecular networks with extended π systems is of interest in modern nanofabrication strategies.^[1–4] The ultimate goal of this bottom-up approach is the development of nanoscale devices and sensors.^[5–9] Typically, molecular networks that undergo structural changes due to an external chemical disturbance^[6] can be the first choice in manufacturing sensors,^[10] electronics^[9] or switches at the single-molecule level.^[5, 11–14] One possible strategy can be employing pH, due to applications in designing experiments in aqueous solutions under potential control,^[15–18] as a knob to manipulate intermolecular hydrogen bonding leading to phase transitions. Based on simple chemical principles, amine (NH₂) groups are hydrogen bond acceptors and donors and it is not unreasonable to expect 2D structures to form based on H-bonds between amine groups from neighboring molecules.^[19–22] However, examples using pure amine-amine hydrogen bonding to construct 2D long range ordered structures have not been reported so far to our knowledge.

In this study, 1,3,5-triaminobenzene (TAB) (Scheme 1) was used as the building block to fabricate a 2D supramolecular structure on the surface of a gold crystal. Aromatic amines are



Scheme 1. Molecular structures of TAB (I) in acidic solution (II) and moderately acidic/neutral solutions (III and IV).

generally protonated on the amino groups. However, TAB is a special case since the first protonation ($pK_1 = 5.5 \pm 0.03$) mainly occurs on the ring carbon atom at room temperature.^[23] Protonation of TAB in acidic and near-neutral solutions generates different species (Scheme 1). The triaminobenzenium cation (Scheme 1, structure III) is the main product of protonation at room temperature at pH \approx 5.5,^[24–25] though a small amount of the amino-protonated species (Scheme 1, structure IV) coexists with carbon ring protonated species (structure III).^[24–25] By decreasing the pH, the three amine groups will eventually all be protonated (Scheme 1, structure II).

We investigated pH-induced structural changes in a TAB monolayer due to the protonation of amine groups and consequently the formation/disruption of hydrogen bonds between neighboring molecules. In our study, we used the electrochemical potential to facilitate the adsorption and formation of the TAB 2D supramolecular structure. Specifically, the electrode potential was set to keep the Au(111) surface negatively charged to drive the adsorption of triaminobenzenium cations (Scheme 1) while pH provided an external chemical stimulus to induce an order/disorder transition in the 2D network of TAB.

In designing the pH-dependent ordered/disordered TAB molecular networks, the first step is to reveal the structural differences of the protonated species at two pH values. We compared the UV/Vis spectra of TAB in acidic (pH \approx 1) and neutral or moderately acidic (pH \approx 5.5) solutions (detailed solution preparation in the Supporting Information, SI). The structure and position of the peaks in the two spectra are different due to different protonation patterns of TAB in the two solutions. In concentrated acid solution, the peak at 272 nm (Figure 1) is evidence that protons attach to amine groups so that TAB is fully protonated.^[24–25] In neutral/moderately acidic solution the peak at 263 nm with a shoulder toward higher wavelengths (Figure 1) is evidence of the presence of a triaminobenzenium ion, where protonation occurs not on the amino groups but

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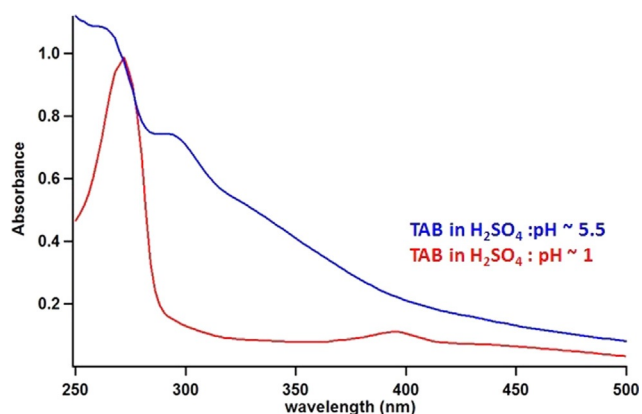


Figure 1. UV/Vis spectra of TAB in acidic (red) and moderately acidic/neutral (blue) solutions.

on the ring carbon atom.^[23–24] In addition to the pH-dependent characteristic UV/Vis spectra, the formation of polyTAB nanosheets in the pH \approx 5.5 solution is another evidence for the presence of triaminobenzenium cations. We observed formation of polyTAB nanosheets (Figure 1, SI), known to occur upon polymerization of triaminobenzenium cations, thus confirming the presence of triaminobenzenium cations in the solution with pH \approx 5.5.^[25–26]

We hypothesized that the protonated amine groups of TAB (Scheme 1, structure II) are not able to form intermolecular H-bonds. Hence, a long-range ordered structure of TAB on the Au(111) surface is unlikely to form in concentrated acidic solution. However, in near neutral solution (pH \approx 5.5) at room temperature, protonation on the ring carbon atom generates species (Scheme 1, structure III) capable of forming intermolecular H-bonds leading to long-range ordered structures of TAB molecules. Based on these hypotheses, we investigated the controllable fabrication of a TAB supramolecular structure on a substrate due to intermolecular amine-amine hydrogen bonding with high molecular precision and employed pH for manipulating ordered/disordered TAB network.

The possible existence of a 2D supramolecular structure of TAB on Au(111) due to intermolecular hydrogen bonding in near neutral solution (pH \approx 5.5, where the first protonation of

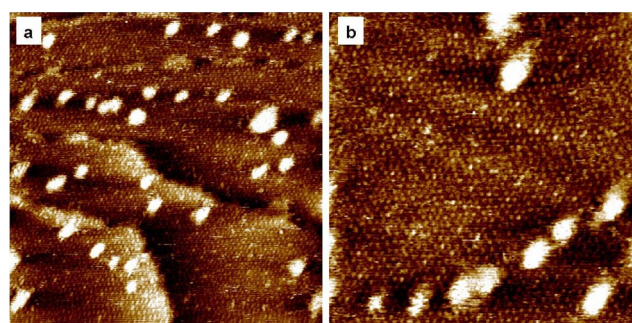


Figure 2. STM images of TAB/H₂SO₄ (pH \approx 5.5) on Au(111), scan area: a) 50 \times 50 nm², b) 30 \times 30 nm². ($E_{\text{surface}} = 0.10 \text{ V}_{\text{SCE}}$, $I_t = 0.1 \text{ nA}$).

TAB happens^[23–24] was revealed using scanning tunneling microscopy (STM) imaging. The TAB monolayer on the Au(111) surface was prepared by adding 1 mm of the supernatant of the TAB/H₂SO₄ (pH \approx 5.5) solution containing transparent polyTAB sheets (Figure 1c, SI) to cover the gold crystal surface under electrochemical potential control ($E_{\text{surface}} = 0.10 \text{ V}_{\text{SCE}}$) at room temperature.

Running STM experiments in an electrochemical environment enables the use of surface potential as an extra controlling parameter to provide a negatively charged Au(111) surface to facilitate the adsorption of the triaminobenzenium cations with a positive charge on the ring carbon (Scheme 1, structure III) and to bring TAB molecules close enough together to form intermolecular amine-amine hydrogen bonds. The large scale STM image (Figure 2) shows that adsorbed TAB molecules form a long range ordered monolayer on Au(111) along with gold islands (bright white features) which appear due to lifting of the gold reconstruction.^[27]

High-resolution STM images (Figures 3a and b) reveal the structural details of the TAB supramolecular network on Au(111) in nearly neutral solution (pH \approx 5.5). The 2D network consists of TAB heptamers: six TAB molecules arranged in a hexagonal pattern with the center occupied by a seventh brighter TAB molecule (indicated with the white ovals in Figure 3a). These heptamers can be considered as the building blocks of the close packed structure on the surface. The estimated length of a TAB molecule is about 6 Å (Figure 3c, de-

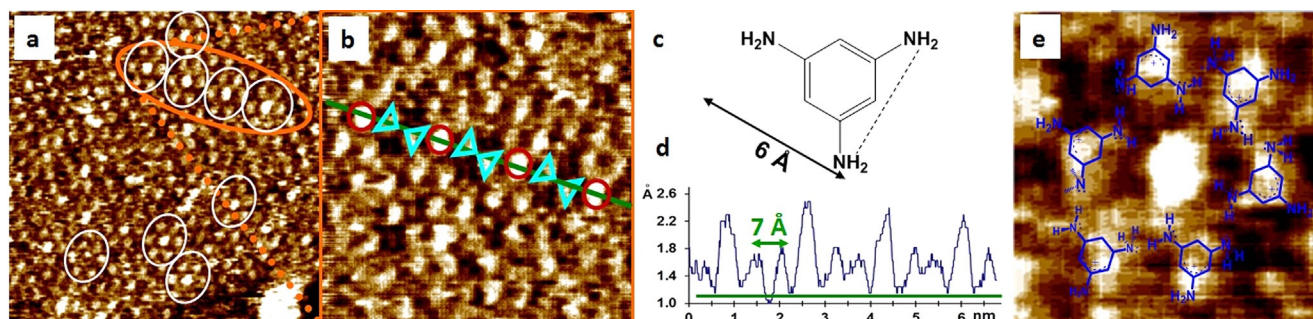


Figure 3. a) STM image of TAB on Au(111)/H₂SO₄ (pH \approx 5.5), $E_{\text{surface}} = 0.10 \text{ V}_{\text{SCE}}$, $I_t = 0.1 \text{ nA}$, Scan area: 15 \times 15 nm², white ovals enclose a hexagonal pattern of six TAB molecules with the center occupied by a seventh TAB molecule; b) 7 \times 7 nm² zoomed-in STM image of (a), cyan triangles and red circles point to TAB molecules with low and high contrast, respectively; c) schematic of a TAB molecule with estimated dimensions; d) cross-section of ordered structure denoted by the green line in image (b), distance between neighboring TAB molecules is \approx 7 Å; e) superimposed TAB molecules on the zoomed-in STM image of (b).

tailed analysis in Figure 2a, SI). The center-to-center distance between neighboring TAB molecules (indicated by cyan triangles in Figure 3b), determined from the cross-section of the ordered structure (Figure 3d), is about 7 Å, which is consistent with the length of a TAB molecule lying flat with its benzene ring parallel to the surface.

The potential of zero charge, where the surface charge is zero, for the electrochemically reconstructed Au(111)-(22×√3) and the Au(111)-(1×1) surfaces are 270 and 230 mV versus SCE, respectively.^[28] Thus, the Au(111) surface at potentials more negative than these values is considered negatively charged. Hence, the driving force for the formation of the supramolecular structure is the negative charge on the Au(111) surface for adsorption of the triaminobenzenium cations (Figure 1, structure III) in heptamer groups followed by hydrogen bonding between amine groups of neighboring TAB molecules in the hexamer ring.

The formation of hexagonal rings is due to the equal-participating amine groups of the six TABs at the vertices in hydrogen bonding. The zoomed-in STM image with superimposed TAB structures drawn based on a real 3D molecular model (Figure 3e) indicates that the six TABs of the hexagonal structure have benzene rings and N—H (H bonds) in the same plane (a clear image of the proposed structure without the STM image in the background can be found in the SI, Figure 2b). Furthermore, TAB molecules from neighboring heptamers can form hydrogen bonds resulting in an almost perfect arrangement of heptamer building blocks in the molecular network (indicated with the orange oval in Figure 3a).

Evidence of intermolecular H-bonding between TAB cations resulting in hexamers is supported by comparing the TAB ordered structure with 2D supramolecular motifs of other benzene derivatives with functional groups in the threefold 1,3,5 positions. Two types of long-range ordered structures, with and without intermolecular H-bonds, are needed for a comparative study. For example, 1,3,5-trimethylbenzene (Figure 4a, inset) forms long-range ordered structures on Au(111) with the benzene ring lying flat on the surface.^[29] Considering the weak intermolecular interactions of methyl groups, the dominant force for long-range ordered structure formation should be the

substrate/adsorbate interactions.^[29] The STM image of the 1,3,5-trimethylbenzene supramolecular structure on Au(111) (Figure 4a) indicates a network with almost the same level of contrast for all the molecules on the surface. On the other hand, 1,3,5-benzenetricarboxylic acid (Figure 4b, inset) is capable of forming a continuous 2D long-range ordered structure on Au(111) (Figure 4b) with hexamer building blocks and via intermolecular hydrogen bonds between neighboring molecules.^[30] Hydrogen bonding mediated by carboxylic acids in the threefold 1,3,5 positions results in the hexamer structure^[30] (Figure 4b) similar to the structure observed for TAB, that is, heptamers (or hexamers including a central TAB) (Figure 3a). Thus, the formation of hexamers in the TAB molecular network on Au(111) is a consequence of the directional nature of hydrogen bonding.

In the 1,3,5-benzenetricarboxylic acid honeycomb structure, most of the central positions in the hexagonal rings are empty (red circles in Figure 4b); a few of them are occupied by a seventh molecule (white circles in Figure 4b). In contrast, in the TAB structure almost all the central positions are occupied by a seventh molecule (white ovals in Figure 3a). The difference in the number of occupied central positions in the two networks can be explained by considering that the positively charged benzene ring of the triaminobenzenium cation is attracted to the negatively charged Au(111) surface facilitating occupation of the central position. However, in 1,3,5-benzenetricarboxylic acid, due to absence of such an adsorbate-substrate driving force, only a few molecules occupy the central position of the hexagonal ring.

The observed difference in contrast in the STM images, and the apparent heights in the cross-section of the ordered structure (Figure 3d), between the TAB molecules constituting the hexagonal ring and the TAB in the center of the ring (Figure 3a and b) suggests that there are two types of TAB molecules in the supramolecular structure on Au(111): TABs that form a hexagonal structure via hydrogen bonding (molecules with low contrast, cyan triangles in Figure 3b) and the central TAB (molecule with high contrast, red circles in Figure 3b). The hexagon acts as a host system for the central TAB (the guest), that is adsorbed flat on the central hole of the hexagon and probably without effective hydrogen bonding to the amine groups of the molecules constituting the hexagon. The possible interaction between the amine groups and the gold surface can dominate the adsorption of the central TAB molecules resulting in almost all the central positions occupied. The lack of such interaction between carboxylic acid groups and the gold substrate results in a honeycomb structure with almost empty central positions. Furthermore, the different contrast of the central TAB and TMA can be explained as due to the fact that central TABs are positively charged species through which tunneling current is different from neutral central TMAs.

To investigate the influence of pH on the TAB network and to compare H-bond formation between neighboring amine groups in acidic and near neutral solutions, STM imaging was carried out in 1 mM TAB/0.05 M H₂SO₄ (pH ≈ 1) solution. A typical large-scale STM image (Figure 5a) shows that the adsorbed TAB molecules do not form any observable ordered structures

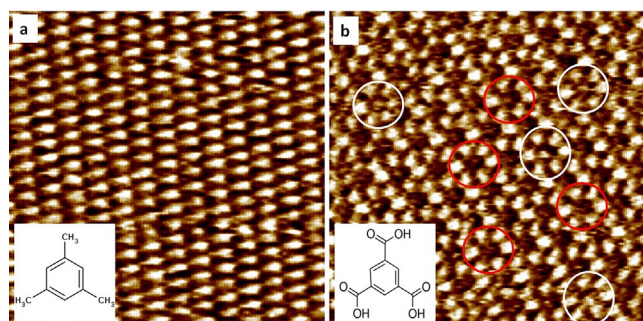


Figure 4. STM images of: a) 1,3,5-trimethylbenzene on Au(111), scan area: $10 \times 10 \text{ nm}^2$, $E_{\text{bias}} = -0.10 \text{ V}$, $I_t = 10 \text{ nA}$, (inset: molecular structure of 1,3,5-trimethylbenzene); b) 1,3,5-benzenetricarboxylic acid/0.05 M H₂SO₄ on Au(111), scan area: $10 \times 10 \text{ nm}^2$, $E_{\text{surface}} = -0.10 \text{ V}_{\text{SCE}}$, and $I_t = 0.1 \text{ nA}$, (inset: molecular structure of 1,3,5-benzenetricarboxylic acid).

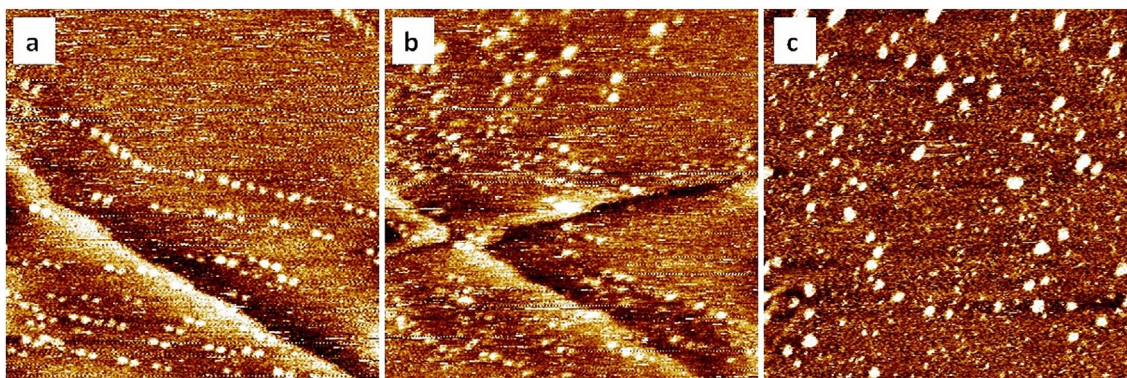


Figure 5. STM images of TAB/0.05 M H₂SO₄ (pH ≈ 1) on Au(111) at: a) $E_{\text{surface}} = -0.10 V_{\text{SCE}}$; b) $E_{\text{surface}} = 0.00 V_{\text{SCE}}$ and c) $E_{\text{surface}} = 0.10 V_{\text{SCE}}$ (scan area 100 × 100 nm², $I_t = 0.1$ nA).

on the negatively charged ($E_{\text{surface}} = -0.10 V_{\text{SCE}}$) Au(111) surface under acidic conditions. STM imaging under the same conditions on more positively charged surfaces ($E_{\text{surface}} = 0.0$ and $+0.10 V_{\text{SCE}}$) did not reveal ordered structures (Figures 5b and c). The lack of long-range ordered structures of TAB molecules in acidic solution may be attributed to the electrostatic repulsion between TAB molecules with the protonated amine groups (Scheme 1, structure II). In case of adsorption of the positively charged TAB molecules on the negatively charged gold substrate, protonated amine groups cannot effectively hydrogen bond between neighboring TAB molecules since the electron lone pair of the nitrogen atom is no longer available as the acceptor in the ammonium ion. Thus, there is an absence of a driving force for the formation of ordered supramolecular TAB structure on the Au(111) surface in acidic solution.

The observation of the assembly of heptamers over the entire surface at pH ≈ 5.5 (Figures 2a and b) suggests intermolecular hydrogen bonding between amine groups. TAB molecules are protonated on the carbon ring (Scheme 1, structure III) at pH ≈ 5.5 leaving the three amine groups available for forming hydrogen bonds with neighboring molecules. Comparing the STM images in acidic and near-neutral solutions indicates that only when the three amine groups of TAB are neutral are they capable of generating long range ordered structures by participating in H-bonding with neighboring TAB molecules. Thus, pH can be utilized to form/disrupt intermolecular H-bonding between neighboring amine groups.

In this work we investigated the formation of 2D supramolecular networks based on pure amine–amine hydrogen bonding on Au(111) at the solid–liquid interface upon the variation of pH. The two different products of proton exchange of 1,3,5-triaminobenzene (TAB) molecules in concentrated and moderately acidic solutions have different capabilities for forming hydrogen bonds between neighboring molecules. In moderately acidic–neutral solution (pH ≈ 5.5), protonation of TAB molecules on the carbon atom of the benzene ring results in species capable of forming intermolecular hydrogen bonds with amine groups from the neighboring TAB molecules. High-resolution STM images reveal the 2D supramolecular structure of TAB molecules with honeycomb structure on Au(111) sur-

face. Lowering the pH causes protonation of the amine groups so that the nitrogen is no longer available for hydrogen bonding and TAB molecules do not form a long range ordered structure on the Au(111) surface. This example demonstrates that pH can be employed to chemically modulate 2D structures applicable in designing molecular sensors and switches.

Experimental Section

Electrochemical Scanning Tunneling Microscopy (EC-STM) Experiments

STM images were obtained with a PicoScan STM system (Molecular Imaging). The PicoStat bipotentiostat (Molecular Imaging) was used to control the surface and tip potential independently. A silver wire and a platinum wire were used as a quasi-reference electrode and counter electrode, respectively, for the neutral solution. For acidic solutions, a platinum wire was used as the quasi-reference electrode instead of Ag. STM tips were prepared by electrochemically etching 0.25 mm diameter tungsten wires in 2 M NaOH solution using a platinum ring electrode. Tips, coated with polyethylene, yielded less than 10 pA Faradic current at 0.1 V bias. All the STM images were obtained under constant current mode. Additional details of the STM experiment can be found under the caption of each image reported. In-situ imaging of 1,3,5-trimethylbenzene was carried out without potential control and mechanically cut gold wire (0.25 mm diameter) was used as tip.

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Keywords: amines · hydrogen bonding · pH · supramolecular chemistry · two-dimensional structures

- [1] M. O. Blunt, J. C. Russell, M. D. C. Gimenez-Lopez, J. P. Garrahan, X. Lin, M. Schroder, N. R. Champness, P. H. Beton, *Science* **2008**, *322*, 1077–1081.
- [2] L. Bartels, *Nat. Chem.* **2010**, *2*, 87–95.
- [3] J. Adisoejoso, K. Tahara, S. Okuhata, S. Lei, Y. Tobe, S. De Feyter, *Angew. Chem. Int. Ed.* **2009**, *48*, 7353–7357; *Angew. Chem.* **2009**, *121*, 7489–7493.

- [4] E. R. Kay, D. A. Leigh, F. Zerbetto, *Angew. Chem. Int. Ed.* **2007**, *46*, 72–191; *Angew. Chem.* **2007**, *119*, 72–196.
- [5] Y. F. He, T. Ye, E. Borguet, *J. Phys. Chem. B* **2002**, *106*, 11264–11271.
- [6] M. Alemani, M. V. Peters, S. Hecht, K. H. Rieder, F. Moresco, L. Grill, *J. Am. Chem. Soc.* **2006**, *128*, 14446–14447.
- [7] J. V. Barth, *Annu. Rev. Phys. Chem. Vol. 58*, **2007**, pp. 375–407.
- [8] J. V. Barth, G. Costantini, K. Kern, *Nature* **2005**, *437*, 671–679.
- [9] T. K. Shimizu, J. Jung, H. Imada, Y. Kim, *Angew. Chem. Int. Ed.* **2014**, *53*, 13729–13733; *Angew. Chem.* **2014**, *126*, 13949–13953.
- [10] L. Piot, R. M. Meudtner, T. El Malah, S. Hecht, P. Samori, *Chem. Eur. J.* **2009**, *15*, 4788–4792.
- [11] F. Rosei, M. Schunack, P. Jiang, A. Gourdon, E. Laegsgaard, I. Stensgaard, C. Joachim, F. Besenbacher, *Science* **2002**, *296*, 328–331.
- [12] G. Pawin, K. L. Wong, K.-Y. Kwon, L. Bartels, *Science* **2006**, *313*, 961–962.
- [13] J. A. Theobald, N. S. Oxtoby, M. A. Phillips, N. R. Champness, P. H. Beton, *Nature* **2003**, *424*, 1029–1031.
- [14] S. De Feyter, F. C. De Schryver, *Chem. Soc. Rev.* **2003**, *32*, 139–150.
- [15] L. C. Giancarlo, G. W. Flynn, *Annu. Rev. Phys. Chem.* **1998**, *49*, 297–336.
- [16] M. GomezLopez, J. A. Preece, J. F. Stoddart, *Nanotechnology* **1996**, *7*, 183–192.
- [17] Q. Yuan, Y. Xing, E. Borguet, *J. Am. Chem. Soc.* **2010**, *132*, 5054–5060.
- [18] Z. Li, M. Smeu, S. Afsari, Y. Xing, M. A. Ratner, E. Borguet, *Angew. Chem. Int. Ed.* **2014**, *53*, 1098–1102; *Angew. Chem.* **2014**, *126*, 1116–1120.
- [19] X. H. Liu, Y. P. Mo, J. Y. Yue, Q. N. Zheng, H. J. Yan, D. Wang, L. J. Wan, *Small* **2014**, *10*, 4934–4939.
- [20] L. Yang, D. Wang, L. J. Wan, *Electrochem. Commun.* **2012**, *17*, 82–84.
- [21] J. C. Swarbrick, B. L. Rogers, N. R. Champness, P. H. Beton, *J. Phys. Chem. B* **2006**, *110*, 6110–6114.
- [22] J. Ma, B. L. Rogers, M. J. Humphry, D. J. Ring, G. Goretzki, N. R. Champness, P. H. Beton, *J. Phys. Chem. B* **2006**, *110*, 12207–12210.
- [23] T. Yamaoka, H. Hosoya, S. Nagakura, *Tetrahedron* **1968**, *24*, 6203–6213.
- [24] T. Yamaoka, H. Hosoya, S. Nagakura, *Tetrahedron* **1970**, *26*, 4125–4130.
- [25] I. Johannsen, J. B. Torrance, A. Nazzari, *Macromolecules* **1989**, *22*, 566–570.
- [26] A. Iwan, D. Sek, *Prog. Polym. Sci.* **2011**, *36*, 1277–1325.
- [27] Y. He, E. Borguet, *J. Phys. Chem. B* **2001**, *105*, 3981–3986.
- [28] S. Wu, J. Lipkowski, O. M. Magnussen, B. M. Ocko, T. Wandlowski, *J. Electroanal. Chem.* **1998**, *446*, 67–77.
- [29] S. Afsari, Z. Li, E. Borguet, *Angew. Chem. Int. Ed.* **2014**, *53*, 9771–9774; *Angew. Chem.* **2014**, *126*, 9929–9932.
- [30] Z. Li, B. Han, L. J. Wan, T. Wandlowski, *Langmuir* **2005**, *21*, 6915–6928.

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