COMMUNICATION

ChemComm
www.rsc.org/chemcomm

STM-based molecular detection of “catch-and-release” of protons for bipyridine bound to phenylene–ethynylene thiol†

Emiko Koyama,*[a] Takao Ishida,[b] Hideo Tokuhisa,[a] Abdelhak Belaissaoui,[a] Yoshinobu Nagawa[a] and Masatoshi Kanesato[a]

[a] *Nanoarchitectonics Research Center (NARC), National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba Central 4, 1-1-1 Higashi, Tsukuba, Ibaraki 305-8562, Japan.*
E-mail: e-koyama@aist.go.jp; Fax: +81 29 861 3029; Tel: +81 29 861 2443
[b] *Institute of Mechanical Systems Engineering (IMSE), AIST, 1-2-1 Namiki, Tsukuba, Ibaraki 305-8564, Japan. E-mail: t-ishida@aist.go.jp; Fax: +81 29 861 7844; Tel: +81 29 861 7203*

Received (in Cambridge, UK) 13th February 2004, Accepted 17th May 2004
First published as an Advance Article on the web 14th June 2004

The protonation/deprotonation response of a novel bipyridine containing (phenylene–ethynylene) thiol adsorbed to a Au surface was investigated with scanning tunneling microscopy (STM), showing reversible changes in the average heights (~ 50 spots) and the height distribution arising from protonation/deprotonation.

The electronic properties of π-conjugated molecules have recently attracted much attention, based largely on their potential applications as molecular wires.[1–4] For example, the electronic properties of an oligo(*p*-phenylene–ethynylene)thiolate, inserted into an alkanethiolate self-assembled monolayer (SAM) on Au has been previously investigated using scanning tunneling microscopy (STM), finding a higher conductivity relative to an alkanethiolate.[1]

On the other hand, 2,2′-bipyridine is one of the most widely used bidentate ligands for coordination of various metal cations[5] as well as protons.[6] The coordination affects electronic states of the conjugation system, resulting in drastic changes in color and changes in redox potential.

Thus, incorporating 2,2′-bipyridine into a π-conjugated system promises to provide a new single-molecule device, in which the conductance is a function of cation coordination. In this study, we have synthesized **1**, in which a bipyridine unit is connected to a conjugated phenylene–ethynylene system. The response of **1** inserted in an octanethiol SAM matrix on Au has been investigated as a function of addition and removal of a proton using STM. The protonation and deprotonation of the bipyridine moiety on the surface was also carefully examined by X-ray photoelectron spectroscopy (XPS) by comparison to the related compound **2** and protonated compound **3** whose crystal structure was determined by X-ray crystallography.

Compound **1** was synthesized in good yield, by a Sonogashira coupling of 5,5′-dibromo-2,2′-bipyridine, which was obtained according to reported procedures,[7,8] with methylthiophenyl acetylene in the presence of $Pd(PPh_3)_4$ catalyst, followed by the oxidation using *meta*-chloroperbenzoic acid to give the corresponding sulfoxide. The Pummerer reaction was then used to convert from the methylsulfinyl to the thiol **1** using trifluoroacetic anhydride.[9] Model compound **2** was obtained by a Sonogashira coupling of 5,5′-dibromo-2,2′-bipyridine with hexylthiophenyl acetylene in the presence of $Pd(PPh_3)_4$ catalyst.

In order to confirm the structure, we have made a single crystal of monoprotonated compound **3**, and performed X-ray crystallographic analysis (Fig. 1).‡ This additionally makes it easier to assign peaks in the XPS spectra. The single crystal was prepared from a CH_2Cl_2 and CH_3CN (9:1) solution containing model compound **2** and 1 equivalent of trifluoromethane sulfonic acid (TfOH). Slow evaporation of the solvent gave a plate-like, red, single crystal. X-ray analysis determined the distances between the proton and the two nitrogen (N1 and N2) atoms in bipyridine are 1.115 and 2.250 Å, respectively, meaning that the N1 nitrogen binds the proton more strongly and almost dominantly, respective to the N2 nitrogen. It is noteworthy that the N atoms in the bicyclic rings of **3** are oriented in the *cis*-position, with a torsional angle between two pyridine rings of 0.1°. This suggest that one nitrogen binds weakly and one nitrogen binds strongly to the proton so as to keep the coplanar structure of the bipyridine moiety.

XPS measurements[10] for cast samples of compounds **2** and **3** on Au were also performed. While, in the case of compound **2**, only one peak at 400.1 eV was observed in N (1s) region, two significant peaks appeared with almost the same intensities at 399.6 and 401.8 eV as referenced to the Au (4f7/2) level at 84.00 eV in the case of compound **3**. Based upon the X-ray structure, these two peaks are assigned to weakly and strongly protonated nitrogens present in the bipyridine rings.

In order to study the protonation/deprotonation of a SAM of compound **1** on Au by XPS and STM, we prepared three samples: sample I was obtained by immersing a Au substrate in a 3 mM ethanol solution of **1** for 24 h. The substrate was removed and rinsed copiously with CH_2Cl_2 to remove any physisorbed **1**; sample II was prepared by subjecting sample prepared as in the case of sample I to a 5 mM solution of TfOH in CH_2Cl_2 and CH_3CN (9:1) for 5 min, followed by rinsing with CH_2Cl_2; sample III was prepared by the further soaking of a sample prepared as in the case of sample II in ethanol for 30 min to deprotonate **1**.

In the case of sample I, formation of a well-ordered SAM of compound **1** was confirmed by STM[11] as shown in Fig. 2A. Two

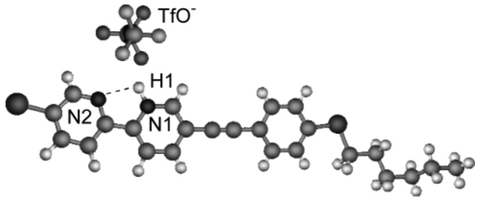


Fig. 1 X-ray crystal structure of **3**. Selected interatomic distances in Å: N1–H1 = 1.115(5), N2–H1 = 2.250(1).

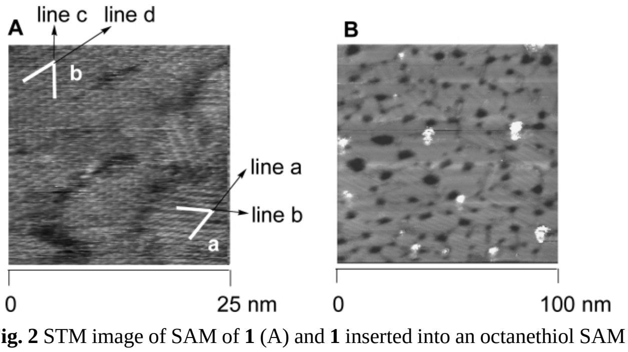


Fig. 2 STM image of SAM of **1** (A) and **1** inserted into an octanethiol SAM (B) on Au. The image was obtained in constant current mode at a bias of 0.5 V and 1.0 V, and a current of 100 pA and 25 pA.

---

† Electronic supplementary information (ESI) available: cross sectional profiles of the STM images before and after the addition of TfOH. See http://www.rsc.org/suppdata/cc/b4/b402251c/

DOI: 10.1039/b402251c

typical orientations were observed in this STM image, labeled a and b in Fig. 2A. For the distinct patterns observed of domain a, the average distances between each spot along lines A and B were approximately 0.8 and 1.0 nm, respectively, and the angle between lines A and B was around ~57°. These results suggest the formation of a $\sqrt{7} \times \sqrt{13}$ R20° structure. In the case of domain b, the distances between each spot along both lines C and D were the same (0.85 nm), and the angle between line C and D was around 60 °, indicating a 3×3 structure. Interestingly, these two domain structures show less-packed patterns than a well ordered $(2\sqrt{3} \times \sqrt{3})$ R30° structure of oligo(*p*-phenylene–ethynylene)thiolates on Au that was reported previously.[12] We expect this less efficient packing will make it easier to protonate/deprotonate the adsorbed molecule.

The spectrum of a self-assembled monolayer of compound **1** on Au (sample I) reveals only one peak at 398.4 eV, which is assigned to the nitrogens of the bipyridine. The protonated SAM (sample II) consists of two peaks at 399.0 and 402.0 eV with almost identical intensities, in good agreement with our observations of compound **3**, as mentioned above. This suggests that under these conditions, bipyridine exists solely as a monoprotonated species, even on the surface. Interestingly, soaking the protonated SAM surface in ethanol (sample III) leads to complete recovery of the peak arising from a nonprotonated bipyridine at 398.7 eV. These results suggest we can control the "catch-and-release" of a proton on the bipyridine rings of compound **1** when present in a SAM using the aforementioned conditions.

Finally, we have investigated the molecular level response to the protonation/deprotonation of the bipyridine in compound **1** on Au by using STM. In this case, because of the difficulty in measuring the absolute height changes of the uniform SAM of compound **1** before and after the addition of TfOH by STM, we utilize a matrix of octanethiol to isolate compound **1** on Au so that apparent height changes upon protonation/deprotonation in the STM images can be measured as a constant. The apparent height difference is potentially a function of physical height, conductance, or both. Compound **1** isolated in a matrix of octanethiol was prepared by soaking the matrix monolayer in 0.14 mM ethanolic solution of compound **1** for 30 min. The STM image of the matrix-isolated **1** is shown in Fig. 2. The images were acquired in constant current mode at a bias of 1.0 V and a current of 25 pA. The bright spots protruding through the matrix layer, which were not observed in the octanethiol-only monolayer, are due to either an isolated molecule or a small collection of compound **1**. The substrate is then processed as described above to effect the "catch-and-release" process. STM images of both the protonated and deprotonated surface were acquired. Typical bright spots from each these three images, are summarized as histograms ($n = 50$) of the apparent height in Fig. 3.

The average heights protruding from the surface, 0.3 nm are clearly lower in the protonated surface (Fig. 3B) relative to the acid-free surfaces, 0.50 and 0.56 nm (Fig. 3A and C). Furthermore, the acid-free surfaces have a larger statistical distribution of apparent heights, 0.180 and 0.213, relative to the protonated surface, 0.143. It is noteworthy that the changes in the average height and the height distribution are almost reversible through the protonation/deprotonation process. A control experiment was performed using a compound incorporating a biphenyl unit instead of the bipyridine unit in compound **1**, resulting in that no change in either the height and the distribution was observed upon the addition of TfOH. This clearly suggests that those changes we observed in the STM images arise from the protonation/deprotonation of the bipyridine.

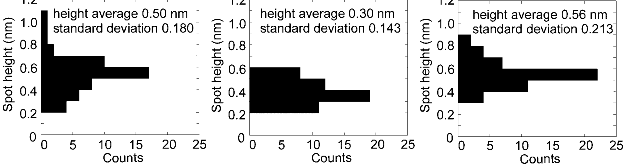
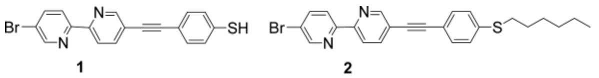


Fig. 3 Histograms of the apparent height of 50 typical bright spots collected from each STM image for **1** inserted into octanethiol SAM on Au, (A) before soaking in TfOH, (B) after soaking in TfOH, and (C) after further soaking in ethanol.



Scheme 1 Structures for phenylene–ethynylene thiol derivatives containing the bipyridine studied here.

This work was partly supported by NEDO under the Nanotechnology Materials Program.

Notes and references

‡ Crystal data for compound **3**: $C_{25}H_{24}N_2O_3S_2F_3Br$, $M = 601.50$, triclinic, $a = 10.50(1)$, $b = 11.15(2)$, and $c = 12.58(2)$ Å, $\alpha = 98.96(7)°$, $\beta = 93.25(6)°$, $\gamma = 106.31(5)°$, $V = 1388.1(3)$ Å^3, $T = 168$ K, space group $P\bar{1}$, $Z = 2$, $\mu = 16.84$ cm^{-1}, 11 489 reflections measured, 5781 unique ($R_{\text{int}} = 0.110$), final R indices $[I > 2t(I)]$ $R_1 = 0.077$, $wR_2 = 0.146$. CCDC number 231280. See http://www.rsc.org/suppdata/cc/b4/b402251c/ for crystallographic data in .cif format.

1 L. A. Bumm, J. J. Arnold, M. T. Cygan, T. D. Dunbar, T. P. Burgin, L. Jones, II, D. L. Allara, J. M. Tour and P. S. Weiss, *Science*, 1996, **271**, 1705–1707.

2 J. Chen, M. A. Reed, A. M. Rawlett and J. M. Tour, *Science*, 1999, **286**, 1550–1552.

3 Z. J. Donhauser, B. A. Mantooth, K. F. Kelly, L. A. Bumm, J. D. Monnell, J. J. Stapleton, D. W. Price Jr., A. M. Rawlett, D. L. Allara, J. M. Tour and P. S. Weiss, *Science*, 2001, **292**, 2303–2307; Z. J. Donhauser, B. A. Mantooth, T. P. Pearl, K. F. Kelly, S. U. Nanayakkara and P. S. Weiss, *Jpn. J. Appl. Phys.*, 2002, **41**, 4871–4877.

4 T. Ishida, W. Mizutani, N. Choi, U. Akiba, M. Fijihira and H. Tokumoto, *J. Phys. Chem. B*, 2000, **104**, 11680–11688; T. Ishida, H. Fukushima, T. Tamaki and H. Tokumoto, *Jpn J. Appl. Phys*, 2003, **42**, 5342–5346.

5 C. Kaes, A. Katz and M. W. Hosseini, *Chem. Rev.*, 2000, **100**, 3553–3590.

6 L. Oresmaa, M. Haukka, P. Vainiotala and T. A. Pakkanen, *J. Org. Chem.*, 2002, **67**, 8216–8219; J.-F. Pan, Z.-K. Chen, S.-J. Chua and W. Huang, *J. Phys. Chem. A*, 2001, **105**, 8775–8781.

7 P.-M. Windscheif and F. Vogtle, *Synthesis*, 1994, 87–92.

8 S. Oae, T. Kawai and N. Furukawa, *Phosphorus Sulfur*, 1987, **34**, 123–132.

9 R. P. Hsung, J. R. Babcock, C. E. D. Chidsey and L. R. Sita, *Tetrahedron Lett.*, 1995, **36**, 4525–4528.

10 XPS spectra were recorded using a Thermo VG Scientific Inc., Theta Probe system with a focused monochromatic Al Kα X-ray source (1486.6 eV). The binding energy was calibrated using the Au ($4f_{7/2}$) peak energy (84.0 eV) as an energy standard. The X-ray power was set at 200 W. The pass energy of the analyser in standard mode was set at 30 eV. The fwhm of Au ($4f_{7/2}$) peak of standard mode and simultaneous angle resolve mode were 0.51 eV.

11 STM images were observed using a Seiko Instruments SPA340 unit under ambient conditions with a typical tunneling current of 20–100 pA and tip biases of +0.5–1. 0V.

12 Al-A. Dhirani, R. W. Zehner, R. P. Hsung, P. Guyot-Sionnest and L. R. Sita, *J. Am. Chem. Soc.*, 1996, **118**, 3319–3320; G. Yang, Y. Qian, C. Engtrakul, L. R. Sita and G.-Y. Liu, *J. Phys. Chem. B*, 2000, **104**, 9059–9062.