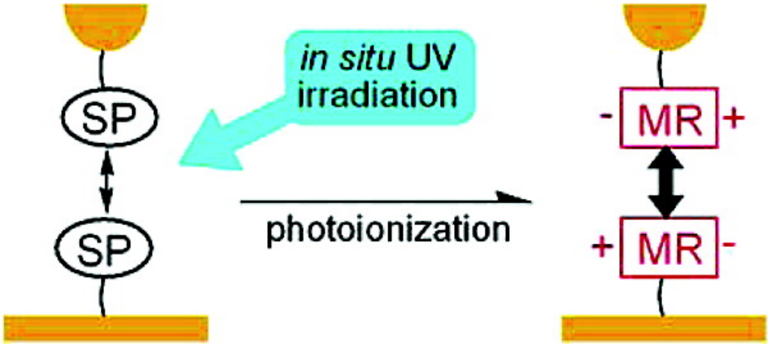
Article

Photoswitching of Single Association Force between a Pair of Photoionizable Spirobenzopyrans

Shinpei Kado, Kaname Yamada, Tomoo Murakami, and Keiichi Kimura

J. Am. Chem. Soc., **2005**, 127 (9), 3026-3030• DOI: 10.1021/ja0443474 • Publication Date (Web): 12 February 2005



Journal of the American Chemical Society is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

JACS ARTICLES

Photoswitching of Single Association Force between a Pair of Photoionizable Spirobenzopyrans

Shinpei Kado, Kaname Yamada, Tomoo Murakami, and Keiichi Kimura*

Contribution from the Department of Applied Chemistry, Faculty of Systems Engineering, Wakayama University, Sakae-dani, Wakayama 640-8510, Japan

Received September 16, 2004; E-mail: kkimura@sys.wakayama-u.ac.jp

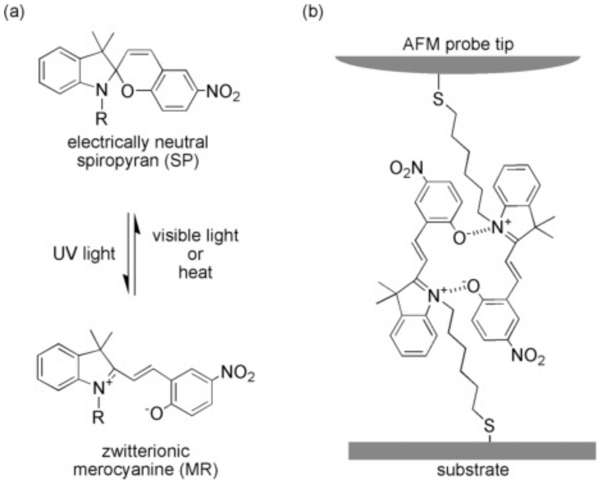
Abstract: We have measured the single intermolecular force of a typical photoionizable molecule, spirobenzopyran, by means of atomic force microscopy, which has proven to be useful in measuring directly single molecular forces. The spirobenzopyran moiety was immobilized covalently on both Au-coated probe tips and substrates by use of a self-assembled monolayer of a hexanethiol derivative incorporating a terminal spirobenzopyran moiety, 1′-(6′-mercaptohexyl)-3′,3′-dimethylindolino-6-nitrospiro-(2*H*-1-benzopyran-2,2′-indoline). Force curve measurements were carried out using the spirobenzopyran-modified probe tip and substrate under dark conditions and in situ UV light irradiation. The adhesion force observed in a polar solvent (i.e., ethanol) was increased substantially under in situ UV light irradiation, which caused photoisomerization of the spirobenzopyran moiety bound to both tip and substrate from its electrically neutral spiropyran form to the corresponding zwitterionic merocyanine one. Statistical analyses of the observed force by autocorrelation technique have revealed that the photoionization enhanced by UV light caused a remarkable increase in the single intermolecular force of the photochromic compound.

Introduction

Photochromic compounds have attracted a great deal of interest since their photoisomerization can be employed to develop photochemically controllable materials for novel photoswitching devices. The photoisomerization, which results in the considerable changes in geometric structure and/or physical properties of the compounds, can be used to control molecular functionalities efficiently by external light stimuli.[1] This also means that the association and assembly of the molecules bearing a photoisomerizable moiety can be manipulated effectively on the molecular level. Then, photoswitching of molecular functionality in organic molecules has been attained by introducing photoisomerizable groups as active constituents into the molecules, aiming at the development of highly functionalized photoresponsive materials and devices.

Several types of photochromic compounds have been used for the design of such photoresponsive molecules so far. One of the important classes in such compounds is the azobenzene derivative. Azobenzene derivatives undergo isomerization from the (*E*)-form to (*Z*)-form by UV light irradiation. This isomerization is accompanied only by the conformation change of the azo group. Another type is a spirobenzopyran (SP) compound. SP undergoes photoisomerization from its electrically neutral closed spiropyran form to its zwitterionic merocyanine (MR) form under UV light irradiation (Scheme 1a).[2,8a] The reverse process can be driven by visible light or heat. The SP form has a benzopyran ring and an indoline moiety linked orthogonally on the spiro-carbon, while the MR one is in planar configuration and has an extended conjugation system of the π-electron

Scheme 1. Photoionization of Photochromic Spirobenzopyran (a) and Schematic Illustration of the Association of Zwitterionic Merocyanine Moieties Immobilized Covalently on Probe Tip and Substrate under In Situ UV Light Irradiation (b)



---

(1) (a) Kimura, K.; Sakamoto, H.; Nakamura, M. *Bull. Chem. Soc. Jpn.* **2003**, *76*, 225−245. (b) Willner, I.; Doron, A.; Katz, E.; Levi, S. *Langmuir* **1996**, *12*, 946−954. (c) Shipway, A. N.; Willner, I. *Acc. Chem. Res.* **2001**, *34*, 421−432. (d) Ipe, B. I.; Mahima, S.; Thomas, K. G. *J. Am. Chem. Soc.* **2003**, *125*, 7174−7175.

(2) (a) Flannery, J. B., Jr. *J. Am. Chem. Soc.* **1968**, *90*, 5660−5671. (b) Song, X.; Zhou, J.; Li, Y.; Tang, Y. *J. Photochem. Photobiol., A* **1995**, *92*, 99−103.

(3) Tachibana, H.; Yamanaka, Y.; Matsumoto, M. *J. Mater. Chem.* **2002**, *12*, 938−942.

(4) (a) Takano, H.; Kenseth, J. R.; Wong, S.-S.; O'Brien, J. C.; Porter, M. D. *Chem. Rev.* **1999**, *99*, 2845−2890. (b) Heinz, W. F.; Hoh, J. H. *Nanotechnology* **1999**, *17*, 143−150. (c) Samorì, B. *Chem.—Eur. J.* **2000**, *6*, 4249−4255. (d) Janshoff, A.; Neitzert, M.; Oberdörfer, Y.; Fuchs, H. *Angew. Chem., Int. Ed.* **2000**, *39*, 3212−3237. (e) Hugel, T.; Seitz, M. *Macromol. Rapid Commun.* **2001**, *22*, 989−1016.

10.1021/ja0443474 CCC: $30.25

between the two rings. In addition to the structural transformation, the photoionization of SP is accompanied by a significant increase in the polarity of the molecule (i.e., molecular dipole), owing to the photogenerated electric charges on MR. Moreover, it is well-known that the photogenerated zwitterionic MR forms associate to each other to form some types of molecular aggregates.[3,8a] One is a head-to-head-type aggregate, and the other is a head-to-tail configuration.[8a]

In the recent decade, atomic force microscopy (AFM) has proven to be a highly sensitive and precise molecular force sensor.[4] AFM force measurements between its probe tip and substrate covered with self-assembled monolayers (SAMs) bearing terminal groups allow the rupture forces of chemical interactions between them to be detected directly. The AFM technique accompanying the immobilization of target molecules to tip and substrate has been successfully applied in measuring directly a variety of single chemical binding forces ranging from biological[5] and artificial[6] specific molecular interactions to polymer chain extensions.[4d,e] Recently, an AFM observation of the single force of polymer stretching induced by photoisomerization of azobenzene units in the polymer chain has been reported.[7]

To the best of our knowledge, there are no AFM force spectroscopic studies on the photoswitching of the intermolecular force in photoionizable organic compounds. We report here that the photochemical reaction of a typical SP compound has been observed directly on a single-molecule level and that photoswitching of the single association force of the molecule can be demonstrated by force measurements under in situ photoirradiation.

Experimental Section

Materials. We synthesized a hexanethiol derivative carrying a terminal SP moiety for covalent attachment of the photoionizable functionality of SP to Au-coated probe tips and substrates (Scheme 1b). Ethanol and toluene of analytical grade were used for the solvents for both chemical modifications and force measurements. Other chemicals were commercially available and used as received.

Synthesis of the SP−Thiol Compound. The syntheses of the SP−thiol compounds have been previously reported.[1b,d] The precursor spirobenzopyran was obtained by the condensation reaction of 1-(6-bromohexyl)-3,3-dimethyl-2-methyleneindoline, which was, in turn, synthesized from 1,6-dibromohexane and 2,3,3-trimethylindolenine, with 5-nitrosalicylaldehyde. The hexanethiol derivative bearing a terminal spirobenzopyran moiety, 1′-(6′-mercaptohexyl)-3′,3′-dimethylindolino-6-nitrospiro-(2*H*-1-benzopyran-2,2′-indoline), was synthesized from the corresponding SP−bromohexane derivative, 1′-(6′-bromohexyl)-3′,3′-dimethylindolino-6-nitrospiro-(2*H*-1-benzopyran-2,2′-indoline), by use of hexamethyldisilathiane according to the literature.[1d]

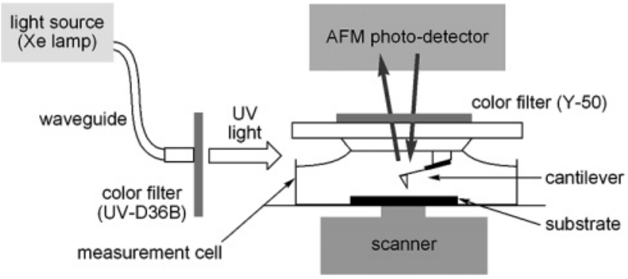


Figure 1. Schematic drawing of experimental setup for AFM force measurements under in situ UV light irradiation.

Chemical Modification. Commercially available V-shaped Si_3N_4 cantilevers (probe tips) coated with Au/Cr ($k = 0.1$ N m^{-1}; Olympus, Tokyo, Japan) were cleaned by immersing into a piranha solution (concentrated H_2SO_4/28% H_2O_2, 7/3, v/v) for 30 min. *Caution: Piranha solutions react violently with organic compounds and should be handled with great care.* After being washed thoroughly with deionized water, the pretreated tips were immersed into a toluene solution containing 1 mM of the ω-SP−hexanethiol for 8 h. Finally, the tips were adequately rinsed with pure toluene and ethanol and then dried in air, resulting in SP-modified tips. Au substrates of about 100 nm thickness were prepared by vacuum evaporation (10^{-6} Torr) of Au (Nilaco, Tokyo, Japan) on natural mica sheets (Nilaco, Tokyo, Japan), freshly cleaved just prior to use. Then, the similar modification procedure mentioned above for the probe tips was applied to the Au/mica substrates to accomplish the covalent bonding of SP functionalities to the substrates.

AFM Force Measurement under Controlled Light Conditions. Adhesion forces were measured at room temperature (ca. 298 K) by an atomic force microscope (SPI3800, Seiko Instruments, Tokyo, Japan). The SP-modified tip and substrate were mounted on the apparatus using a glass liquid cell. Photochemical isomerization of the spiropyran form to the merocyanine one, bound to both the tip and the substrate, was accomplished by UV light irradiation from outside of the cell. Schematic illustration of our experimental setup is drawn in Figure 1. Photoirradiation was made in situ to the AFM cell by using UV light (300−400 nm), which was obtained by passing light from a Xe lamp (L8388-04, Hamamatsu Photonics) equipped with a quartz waveguide through a color filter (UV-D36B, Asahi Techno Glass). A 500 nm cutoff filter (Y-50, Asahi Techno Glass) was placed in front of a position-sensitive detector in order to prevent the UV light from disturbing the photodetection of the cantilever's deflection. For dark conditions, the liquid cell was protected from room light by a shield cover. The force measurements were performed repeatedly in ethanol >100 times for each tip/substrate combination under the different light conditions. The single binding force was evaluated with autocorrelation analysis from histograms of more than 300 values of the adhesion force obtained by combining three data sets of each SP-modified tip/substrate combination.

Results and Discussion

UV Light Effect on Adhesion Force. To investigate the UV light effect on the adhesion force between the SP-modified tip and substrate, AFM force measurements were carried out under dark and UV light conditions in ethanol, which is a typical polar solvent used for the photochemical studies on SP photoisomerization. We obtained the histograms of the adhesion force by

---

(5) (a) Florin, E.-L.; Moy, V. T.; Gaub, H. E. *Science* **1994**, *264*, 415−417. (b) Lee, G. U.; Kidwell, D. A.; Colton, R. J. *Langmuir* **1994**, *10*, 354−357. (c) Lee, G. U.; Chrisey, L. A.; Colton, R. J. *Science* **1994**, *266*, 771−773. (d) Boland, T.; Ratner, B. D. *Proc. Natl. Acad. Sci. U.S.A.* **1995**, *92*, 5297−5301. (e) Tromas, C.; Rojo, J.; de la Fuente, J. M.; Barrientos, A. G.; García, R.; Penadés, S. *Angew. Chem., Int. Ed.* **2001**, *40*, 3052−3055. (f) Rigby-Singleton, S. M.; Allen, S.; Davies, M. C.; Roberts, C. J.; Tendler, S. J. B.; Williams, P. M. *J. Chem. Soc., Perkin Trans.* **2002**, *2*, 1722−1727.

(6) (a) Conti, M.; Falini, G.; Samorì, B. *Angew. Chem., Int. Ed.* **2000**, *39*, 215−218. (b) Schönherr, H.; Beulen, M. W. J.; Bügler, J.; Huskens, J.; van Veggel, F. C. J. M.; Reinhoudt, D. N.; Vancso, G. J. *J. Am. Chem. Soc.* **2000**, *122*, 4963−4967. (c) Zapotoczny, S.; Auletta, T.; de Jong, M. R.; Schönherr, H.; Huskens, J.; van Veggel, F. C. J. M.; Reinhoudt, D. N.; Vancso, G. J. *Langmuir* **2002**, *18*, 6988−6994. (d) Auletta, T.; de Jong, M. R.; Mulder, A.; van Veggel, F. C. J. M.; Huskens, J.; Reinhoudt, R. N.; Zou, S.; Zapotoczny, S.; Schönherr, H.; Vancso, G. J.; Kuipers, L. *J. Am. Chem. Soc.* **2004**, *126*, 1577−1584. (e) Skulason, H.; Frisbie, C. D. *J. Am. Chem. Soc.* **2002**, *124*, 15125−15133. (f) Kado, S.; Kimura, K. *J. Am. Chem. Soc.* **2003**, *125*, 4560−4564.

(7) Hugel, T.; Holland, N. B.; Cattani, A.; Moroder, L.; Seitz, M.; Gaub, H. E. *Science* **2002**, *296*, 1103−1106.

(8) (a) Berkovic, G.; Krongauz, V.; Weiss, V. *Chem. Rev.* **2000**, *100*, 1741−1754. (b) Ichimura, K. *Chem. Rev.* **2000**, *100*, 1847−1874. (c) Tamai, N.; Miyasaka, H. *Chem. Rev.* **2000**, *100*, 1875−1890. (d) Takahashi, H.; Yoda, K.; Isaka, H.; Ohzeki, T.; Sakaino, Y. *Chem. Phys. Lett.* **1987**, *140*, 90−94. (e) Takahashi, H.; Murakawa, M.; Sakaino, Y.; Ohzeki, T.; Abe, J.; Yamada, O. *J. Photochem. Photobiol., A* **1988**, *45*, 233−241.

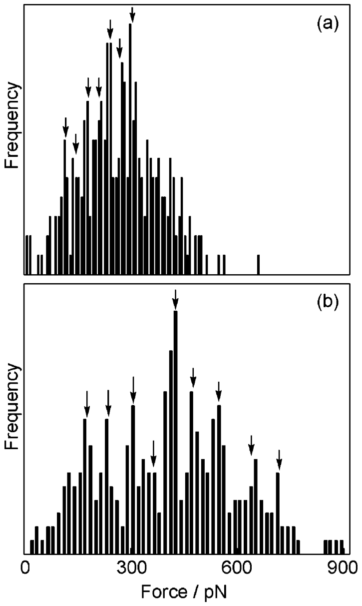


Figure 2. Histograms of adhesion forces observed in ethanol between SP-modified tip and substrate under dark conditions (a) and UV light irradiation (b). The data set plotted was obtained with three different tip/substrate combinations. The average values of adhesion forces were 260 and 390 pN under dark conditions and UV light irradiation, respectively. The arrows in parts a and b indicate the peaks corresponding to the integral multiples of the single forces of 30 and 60 pN, respectively.

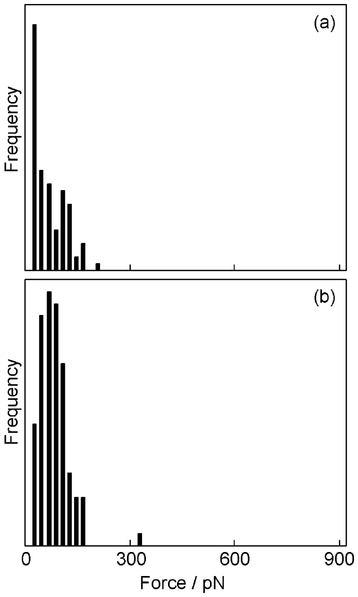


Figure 3. Histograms of adhesion forces observed in ethanol between unmodified tip and substrate under dark conditions (a) and UV light irradiation (b).

combining data sets of repetitive force measurements for three tip/substrate combinations under dark and UV light irradiation (Figure 2). The comparison of the histograms indicates that the adhesion force was increased significantly under in situ UV light irradiation. Such an increase in the adhesion force induced by UV light was observed for six different combinations of SP-modified tip/substrate.

We also carried out control experiments similar to the aforementioned force measurements using unmodified probe tips instead of the SP-modified tips. In contrast to the SP-modified tips, the external UV light caused no significant increase in the adhesion force observed with the unmodified tips (Figure 3). Furthermore, when unmodified tips were used, the adhesion force under dark conditions was much smaller than that obtained with the SP-modified tips, suggesting that there are not any noticeable interactions between the unmodified tip and SP-modified substrate. Then, the force observed between the SP-modified tip and substrate under dark conditions (Figure 2a) can be assigned to the interaction of SP moieties. These results obtained from the control experiments without SP moieties on the tip indicate that the SP moieties immobilized on both the tip and the substrate are crucial for the adhesion force enhanced under UV light irradiation and also that other effects induced by UV light, such as thermal excitation, would be less dominant for the adhesion force measured under our experimental conditions. The photochromic behavior of SP derivatives has been investigated in solution as well as in various matrixes, such as liquid crystals,[8b] Langmuir−Blodgett (LB) films,[3] and SAMs.[1b−d] An SP−SAM formed on polycrystalline Au electrodes similar to that used in this study has been already utilized for the photoswitching of electrochemical reactions based on its photoionization reaction in the monolayer.[1b,c] Thus, the photoinduced increase in the adhesion force discussed here was caused mainly by the photoionization of SP moieties bound covalently to the tip and substrate. As is well-known, the zwitterionic MR isomers exhibit a tendency to aggregate to each other in stack-like arrangement.[8a] Even in the monolayer state, photogenerated MRs are able to associate to form aggregates. For example, it has been previously reported that photoresponsive colloidal silica particles, which were covered with the SP functionality through a silane monolayer, aggregate by irradiating UV light onto the colloid dispersion.[9] Therefore, we conclude reasonably that the force observed under in situ UV light irradiation can be attributed to the intermolecular force based on the association of the zwitterionic MR forms photogenerated as depicted schematically in Scheme 1b. The spectroscopic studies on the photochromic reaction of SP derivatives in solution have revealed that various isomers of the open MR exist.[8c−e] The structure of MR in Scheme 1b is one of the more stable isomers. The nature of the interaction between MRs bound on tip and substrate is probably electrostatic, owing to the large polarity of MR and presumably additional π-stacking by aromatic rings.

Solvent Effect on Adhesion Force. We also examined the UV light effect on the pull-off force between the SP-modified tip and substrate measured in a nonpolar solvent (toluene). Figure 4 shows the histograms of the adhesion force observed in toluene under different light conditions using the SP-modified tip and substrate. As can be seen, UV light irradiation did not cause any noticeable increase in the adhesion force in toluene.

Photochromism of SP compounds in homogeneous solution has been studied extensively in a variety of solvents. The formation of aggregates of photogenerated MR forms is encouraged more strongly in a nonpolar solvent than in a polar one.[2] Thus, no significant effect of UV light on the adhesion force in toluene seems to be apparently in conflict with that expected from the nature of MRs formed by the photoisomerization of SPs in homogeneous solution. However, the photo-

---

(9) (a) Ueda, M.; Kim, H. B.; Ichimura, K. *J. Mater. Chem.* **1994**, *4*, 883−889. (b) Ueda, M.; Kudo, K.; Ichimura, K. *J. Mater. Chem.* **1995**, *5*, 1007−1011.

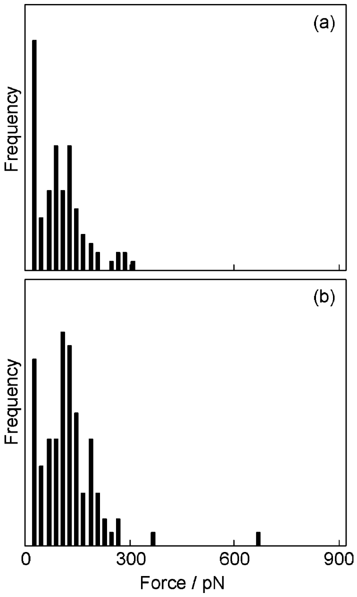


Figure 4. Histograms of adhesion forces observed in toluene between SP-modified tip and substrate under dark conditions (a) and UV light irradiation (b).

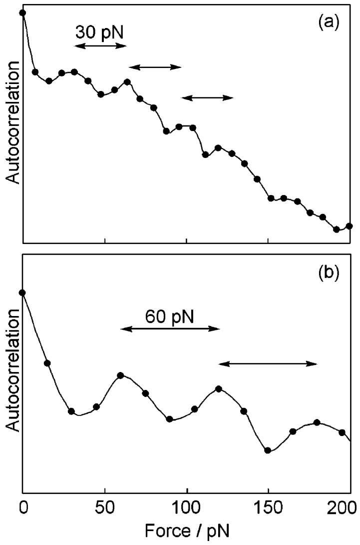


Figure 5. Autocorrelation analysis of histograms (Figure 2) of adhesion forces observed between SP-modified tip and SP-modified substrate in ethanol under dark conditions (a) and UV light irradiation (b).

isomerization of SP to MR is accelerated efficiently in polar solvents, such as alcohol, due to the stabilization of zwitterionic MR by solvents. In contrast, MR is not stable in nonpolar solvents, and therefore, the rate constant of the reverse reaction (i.e., the isomerization of MR back to SP) is much higher than that in polar solvent. The UV-induced isomerization of SP to MR starts with scission of covalent bonding between the spiro-carbon and O atoms, followed by the further transformation to its stabilized open isomers. Hence, the results shown in Figure 4 would be attributed to the extremely low stability of the MR form immobilized on surfaces in toluene. The photogenerated open MR forms could not be in favorable configurations for interacting during the contact between the tip and substrate, leading to no enhancement of the adhesion force under UV light conditions.

Photoswitching of Single Force. The autocorrelation analysis of the pull-off forces has been applied successfully for evaluating the single rupture force for various molecule pairs.[5a,e,6] The single force between the photoionizable SPs can be evaluated by autocorrelation analyses of the histograms of the adhesion forces measured repeatedly. The autocorrelations calculated from the histograms (Figure 2) are plotted in Figure 5. Under dark conditions, there is a distinct periodicity of 30 pN (Figure 5a), whereas the peaks with an appreciably large period of 60 pN are seen very clearly in the autocorrelation obtained from the adhesion forces under UV light condition (Figure 5b).[10] Obviously, the period for the autocorrelation analyses was altered markedly by in situ UV light irradiation. The arrows in Figure 2 indicate the peaks corresponding to multiples of these periods. Most of the SPs on the tip and substrate would undergo photoionization to MRs under such conditions. Hence, the period of 60 pN in Figure 5b can be assigned to the electrostatic force based on association between the photogenerated zwitterionic MRs. On the other hand, the much smaller single force of 30 pN under dark conditions could be assigned to the intrinsic van der Waals interaction between the SPs since they hardly undergo the isomerization to ionic MRs under such conditions, being still in their electrically neutral forms.

Isomerization of SP in SAM. We tried to evaluate the photoisomerization ratio in the SPs bound covalently on the tip and substrate by UV light from the single forces between two photoionizable functionalities and the average adhesion forces described above. In the autocorrelation method used here for estimating the single forces, the observed adhesion force, F, can be given by the product of the single force, F_s, and the number of bonds formed, N.

$$F = NF_s \tag{1}$$

Therefore, the relationship can be used to calculate the average number of molecular interactions formed between the probe tip and substrate. Dividing the average values of the adhesion forces by the corresponding single forces afforded average numbers of 8.7 and 6.5 under dark and UV light conditions, respectively. The number of the interactions formed was altered undoubtedly by UV light irradiation, indicating that the dominant interaction force observed here was switched by UV light. The average number of 8.7 could correspond to the number of SPs, N_{SP}, and then that of 6.5 could be equated to the average number of the MR forms photogenerated, N_{MR}.

The contact area between the tip and substrate can be estimated by application of the Johnson–Kendall–Roberts (JKR) model[11] for the contact mechanics in the adhesion force measured by AFM.[6e,12] Using the adhesion force determined experimentally, the tip radius (R = 40 nm) provided by the manufacturer, and the elastic module of ~1 GPa, the contact

---

(10) The autocorrelation analysis of another data set of the force obtained from three tip/substrate combinations afforded similar photoinduced changes in the periods, which were estimated to be 30 and 52 pN for dark and UV light conditions, respectively. The difference of the periods (in comparison with the values in the text, 30 and 60 pN for dark and UV light conditions) was within experimental errors in our force measurements.

(11) Johnson, K. L.; Kendall, K.; Roberts, A. D. *Proc. R. Soc. London, Ser. A* **1971**, *324*, 301–320.

(12) (a) Noy, A.; Frisbie, C. D.; Rozsnyai, L. F.; Wrighton, M. S.; Lieber, C. M. *J. Am. Chem. Soc.* **1995**, *117*, 7943–7951. (b) van der Vegte, E. W.; Hadziioannou, G. *Langmuir* **1997**, *13*, 4357–4368.

area can be estimated to be ∼12 nm^2. Then, the number of SP moieties in the contact area can be calculated based on the area occupied by the spirobenzopyran molecule, with an area of 0.8 nm^2/molecule, amounting to ∼15 SP molecules. Even though the calculation is rough, the estimated value is in reasonable agreement with the average numbers computed from the average of the adhesion force and the single forces based on eq 1. This supports sufficiently our conclusion that the force values revealed by the autocorrelation analyses (the periodicities seen in Figure 5) can be assigned to the single force between the photoionizable moieties.

When the constancy in the contact area and probability of bond formation between the tip and substrate under different light conditions are assumed, the ratio of $N_{\mathrm{MR}}/N_{\mathrm{SP}}$ could virtually correspond to the proportion of photogenerated MRs to SPs in their monolayer states. Thus, the photoisomerization ratio of the photogenerated MR to SP ($N_{\mathrm{MR}}/N_{\mathrm{SP}}$) was roughly estimated to be 75%, which is higher than that expected for SP derivatives in homogeneous solution.[2,13] It is well-known that photochromic reaction of spiropyrans is affected by properties of matrixes where it occurs.[3,8b] Such enhancement in the photoisomerization (i.e., the stabilization of MRs) has been also found in the systems containing LB films, polymers, and silane monolayers of SP compounds.[13] Therefore, the ratio of isomers in the SP photoionization estimated here may be explained by the different states of SPs (i.e., matrix effect[8b,14]).

Conclusion

We have measured the intermolecular force between the photoionizable spirobenzopyran derivative, a well-known photochromic molecule, by means of AFM using the Au-coated probe tip and substrate covered with the SAM bearing the terminal functionality of spirobenzopyran. The increase in the adhesion force induced by in situ UV light irradiation was detected in ethanol. Furthermore, photoswitching of the observed force by UV light was revealed by autocorrelation analysis of histograms of the adhesion force obtained by repetitive force measurement under dark and in situ UV light conditions. We estimated the individual force of the photoionizable functionality to be 30 and 60 pN for dark and in situ UV light conditions, respectively. The number of the interacting photoresponsive moieties immobilized covalently on the tip and substrate, estimated from the single forces and averages of the adhesion force, was in good agreement with that of the moieties within the contact area calculated from the surface density in SAMs based on the contact mechanics model of the JKR theory. Consequently, we conclude that the photochemical change in the single intermolecular force of the spirobenzopyran derivative based on its photoionization to its zwitterionic merocyanine form was observed directly by AFM, and also that the photoionization behavior on the single-molecule level was realized. This could indicate new possibilities of the AFM force spectroscopic technique for elucidating in situ light-stimulated changes in the assembly and functionality of photoresponsive molecules at the molecular level.

JA0443474

---

(13) Galvin, J. M.; Schuster, G. B. *Supramol. Sci.* **1998**, *5*, 89−100.
(14) Schomburg, C.; Wark, M.; Rohlfing, Y.; Schulz-Ekloff, G.; Wöhrle, D. *J. Mater. Chem.* **2001**, *11*, 2014−2021.