Electronic Supplementary Information (ESI)

Repeated photoswitching performance of azobenzenes adsorbed on gold surfaces: A balance between space, intermolecular interactions, and phase separation

Mitsuyuki Kaneta,[a] Takumu Honda,[a] Ken Onda,[b,c] and Mina Han*[a,d]

[a] *Department of Chemistry and Department of Electronic Chemistry, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226-8502, Japan.*
[b] *School of Science, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226-8502, Japan.*
[c] *JST, PRESTO, 4-1-8 Honcho, Kawaguchi 332-0012, Japan*
[d] *Department of Chemistry and Biotechnology, Tottori University, 4-101 Koyama Minami, Tottori 680-8552, Japan.*

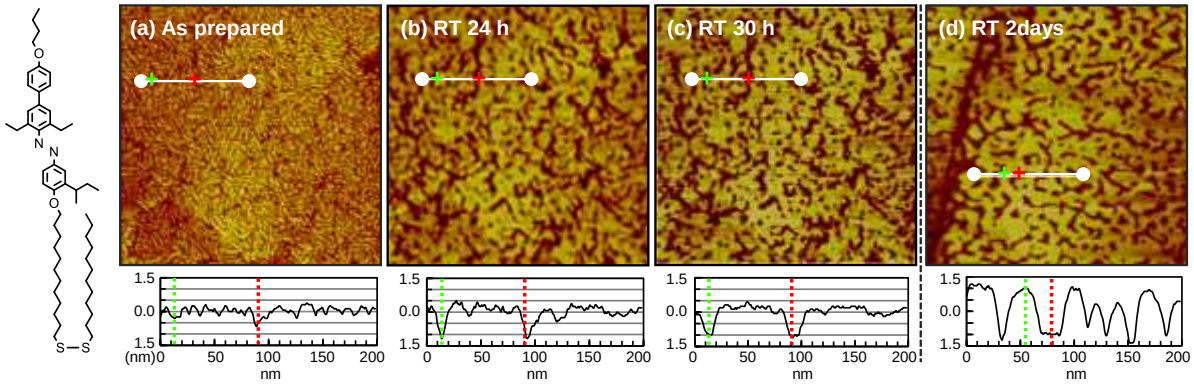

Figure S1 (a)-(c) AFM images and height profiles continuously monitored without changing the position of the Et-SS (ortho-alkylated azobenzene) sample for 30 hours under 18-19 ^{o}C and 32-35% relative humidity condition. The height contrast between the brighter and darker regions becomes more pronounced as small worm-like domains merge with each other. (d) AFM image of phase-separated Et-SS SAMs on an Au(111) surface after dark incubation for 2 days.

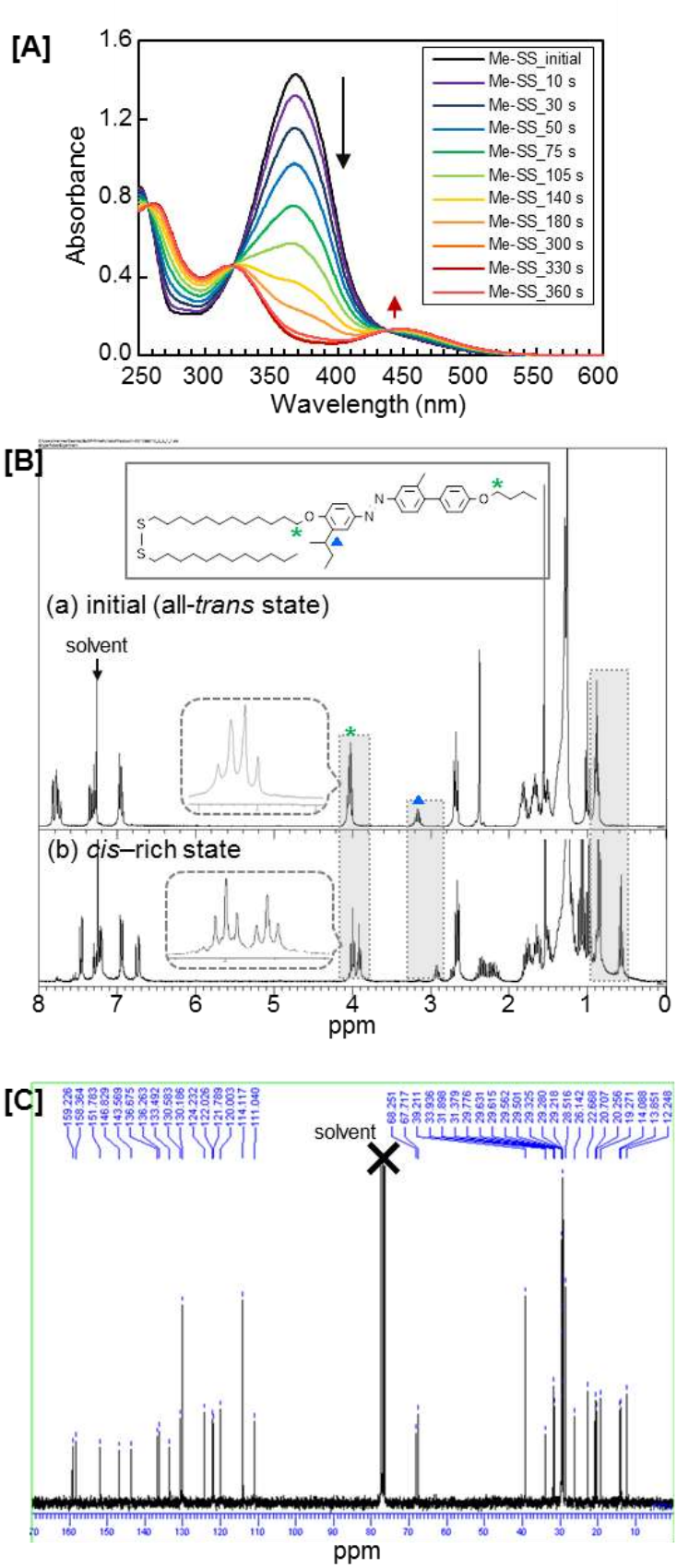

Figure S2 [A] UV-vis absorption spectral changes of Me-SS in dichloromethane solution as a function of exposure time of 365-nm light (~0.3 mW/cm^2). [B] ^{1}H NMR spectral changes of Me-SS in $CDCl_3$ before (initial: all-*trans* state) and after (*cis*-rich state) UV light irradiation. [C] ^{13}C NMR spectrum of all-*trans* Me-SS in $CDCl_3$.

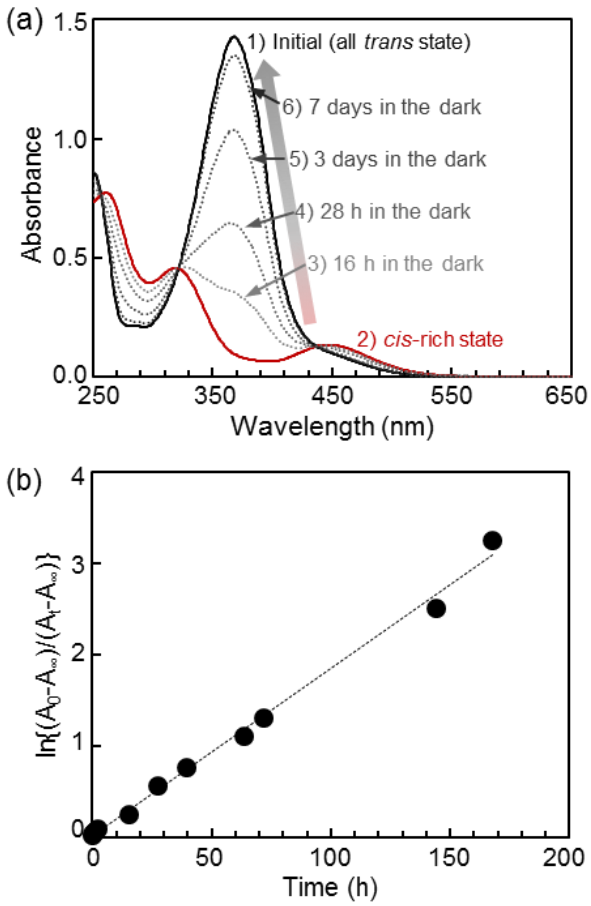

Figure S3 (a) Absorption spectral changes of Me-SS SAMs as a function of thermal *cis*-to-*trans* isomerization time after 365-nm light. (b) First-order plot for thermal *cis*-to-*trans* isomerization of Me-SS in dichloromethane. The first-order rate constant of Me-SS was found to be approximately 0.018 h^{-1}.

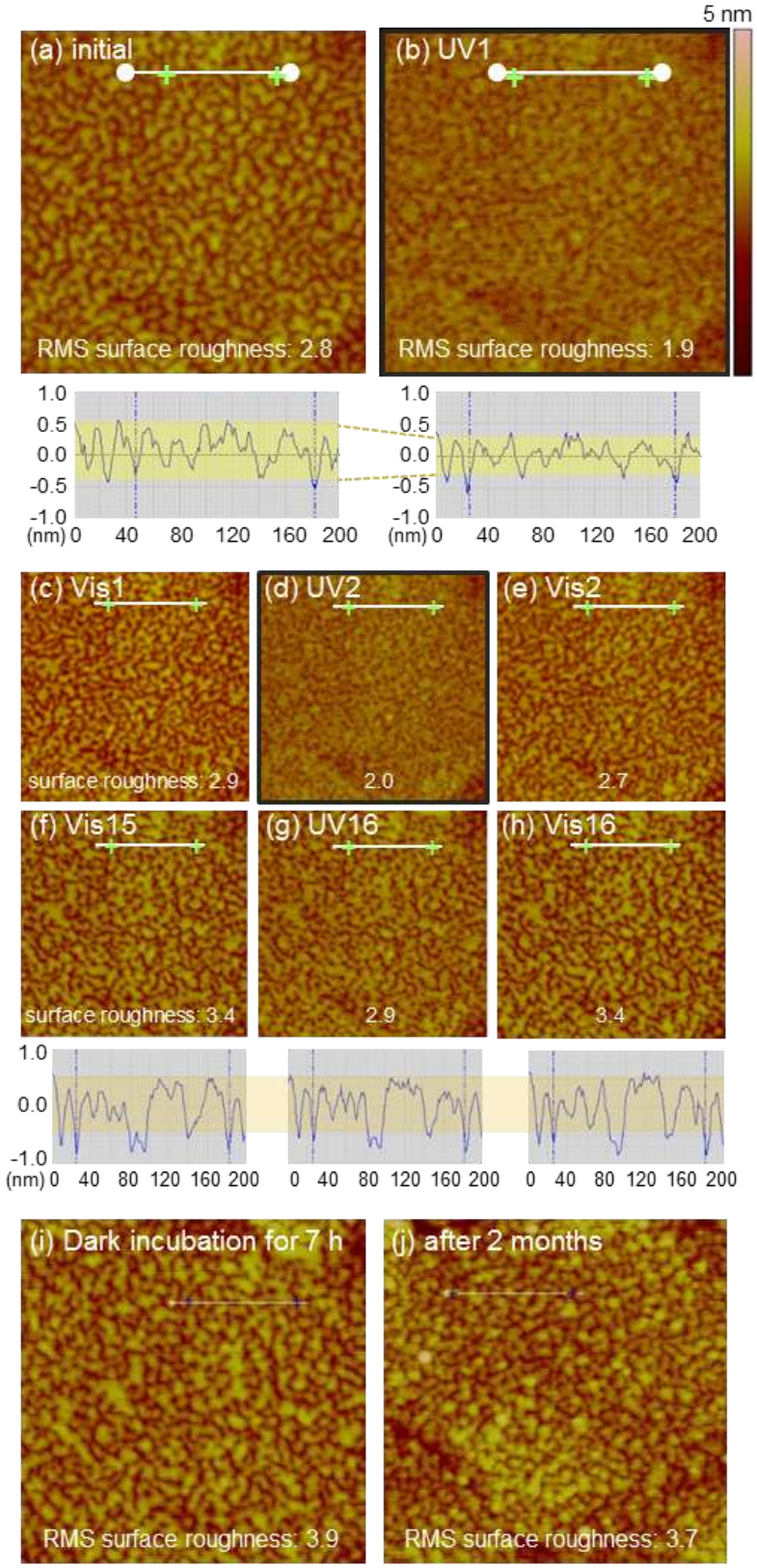

Figure S4 AFM topographic images, height profiles, root mean-square (RMS) surface roughness values (Å) of Me-SS SAMs on an Au(111) surface as a function of alternating irradiation with 365-nm and 436-nm light. The dimension of the respective images (a-h) is 400 × 400 nm^2. The respective RMS surface roughness values (Å) were calculated on the flat area of 100 × 100 nm^2.