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Electronic supplementary information
Quantized Conductance Behaviour Observed in an Atomic Switch using Triptycene-based Polymer

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1: AFM image of a TBAP film on an ITO substrate:

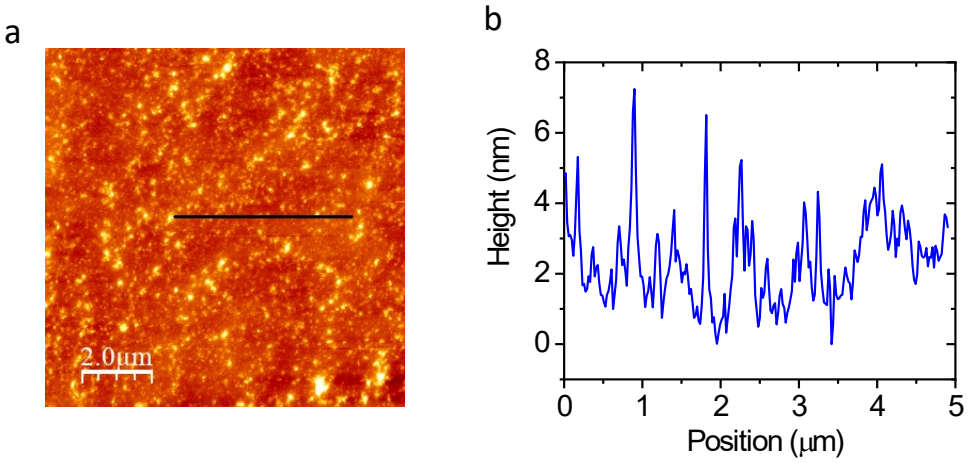

Figure S1: (a) AFM topography image (10 μm × 10 μm) of a 100 nm thick TBAP film spin coated on an ITO substrate, and (b) the line profile across the black line in (a). The surface roughness is estimated to 3 nm.

2: Effect of film thickness on the switching behaviour of the TBAP atomic switch:

In ECM devices, the thickness of a switching layer plays an important role in determining the resistive switching behaviour, because a metal filament is formed through the switching layer.[1] In

this work, the thickness of the TBAP film also has a predominant effect on the resistive switching, especially on the forming process.

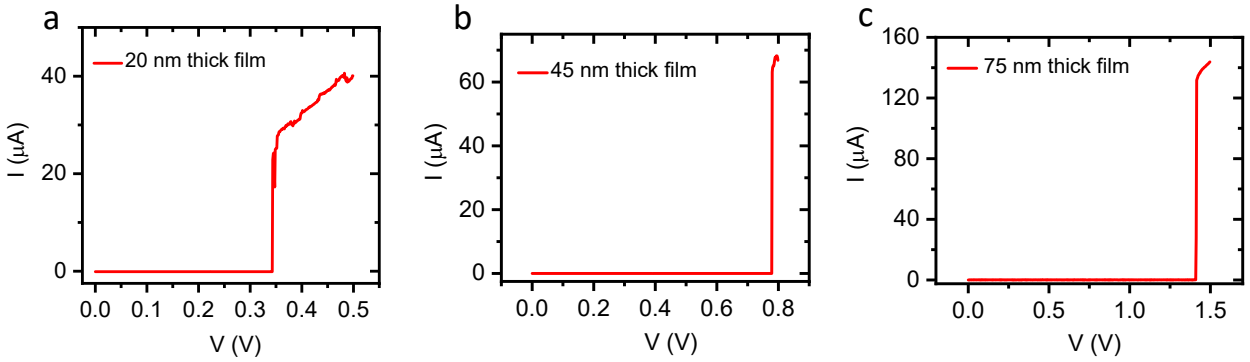

Figure S2: Typical *I-V* curves at the first voltage sweep, measured for TBAP films with thickness (a) 20 nm (b) 45 nm (c) 75 nm.

Figure S2 shows the typical *I-V* curves at the first voltage sweep, measured for TBAP films with three different film thicknesses of 20, 45, and 75 nm respectively, which correspond to the forming process. We see that the forming voltage increased with increasing thickness of the TBAP film: 0.35 V for 20 nm (a), 0.78 V for 45 nm (b), and 1.4 V for 75 nm (c). We also measured the TBAP film with a thickness of 115 nm, but no forming process was observed for the bias voltage range employed. It was found that the 20 nm-thick TBAP film is difficult to maintain stable switching for repeated sweeps, and it is likely to short-circuit after some sweeps. The 75 nm-thick film needs higher voltages for resistive switching, giving rise to an abrupt jump to the ON state. As a result, it is difficult to observe quantized conductance states below $10G_0$ with this film thickness. Thus, we concluded that there is an optimum thickness for the TBAP film and the film with thickness of 45 nm is most suitable for realizing quantized conductance with voltage sweep conditions used.

3: *I-V* characteristics of the TBAP atomic switch under vacuum conditions:

The C-AFM measurements were also performed under vacuum conditions of 4×10^3 Pa. *I-V* curves were measured for consecutive 43 voltage sweeps including the forming process and subsequent resistive switching, as shown in Figure S3a. The forming voltage was around 1 V, which is a little higher than that obtained under atmospheric conditions. Although the SET voltage decreased slowly with increasing voltage sweeps, it ranged from 0.15 to 0.3 V after the 30th voltage sweep, which is almost the same as the SET voltages in atmosphere.

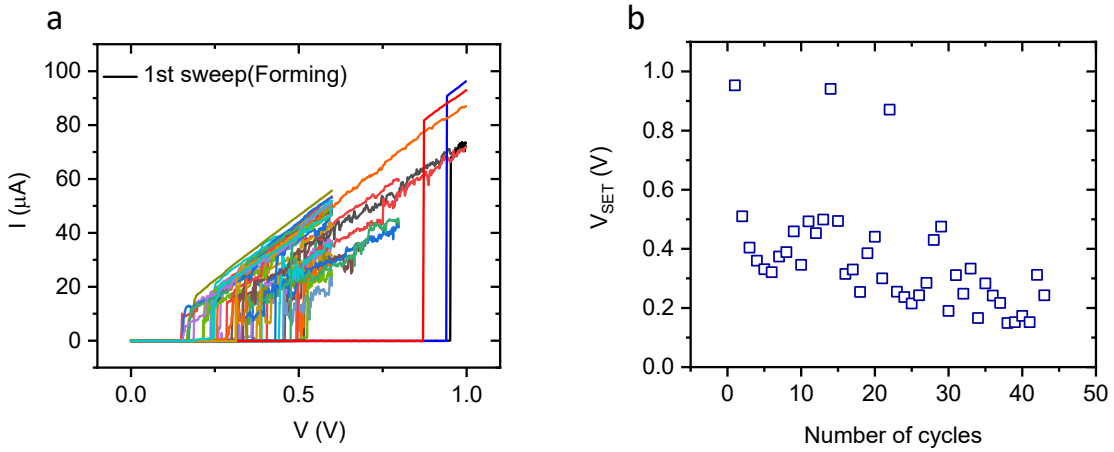

Figure S3: (a) Forming and subsequent switching behaviours measured for the TBAP switch under vacuum conditions of 4 $\times 10^3$ Pa. *I-V* curves were obtained for consecutive 43 voltage sweeps. (b) The SET voltages plotted as a function of the number of the voltage sweeps, extracted from the *I-V* curves of (a).

This behaviour is completely different from polyethylene oxide (PEO)-based atomic switches. In the PEO switches, the SET voltage increases apparently with decreasing ambient pressure down to 10 Pa, and finally the switch exhibits no switching behaviour under similar vacuum conditions of ~10^{-3} Pa.[2,3] Thus, we concluded that the TBAP-based atomic switch is not much affected by moisture absorption and can show stable resistive switching regardless of varied ambient pressures.

4: Quantized conductance states of the TBAP atomic switch:

Figure S4a shows conductance (in units of G_0) - voltage (*G-V*) curves of TBAP atomic switch measured for consecutive 11 voltage sweeps in vacuum. On sweeping the bias voltage to a fixed stop voltage of 0.6V, quantized conductance states of nearly $1G_0$ were observed repeatedly. This result suggests that the TBAP atomic switch could realize the same quantized conductance states under the identical bias condition. Figure S4b plots a *G-V* curve obtained by increasing the stop voltage to 1 V. In addition to $1G_0$, a higher quantized conductance state can be observed.

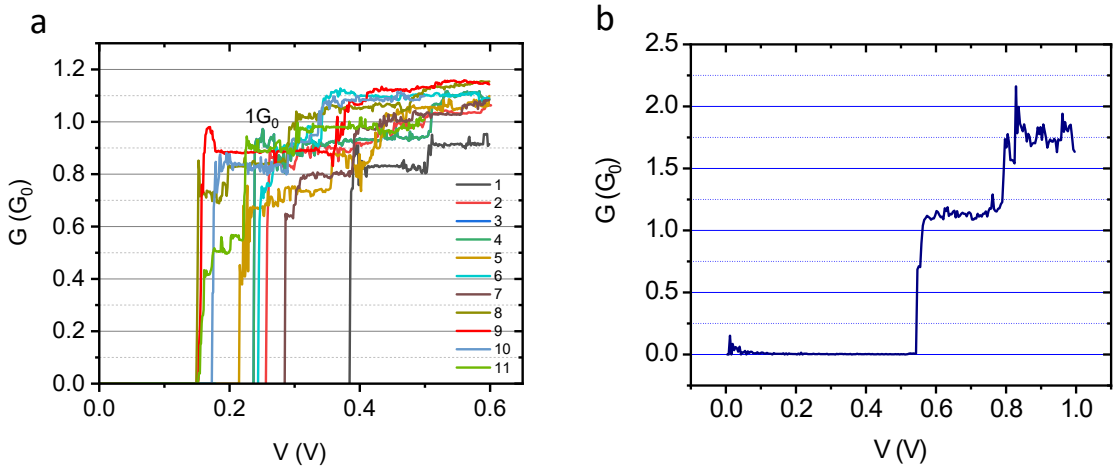

Figure S4: Conductance (in units of G_0) – voltage (G-V) curves measured for TBAP atomic switch. (a) consecutive 11 sweeps up to 0.6 V. (b) single sweep up to 1 V. The bias voltage was swept to the Ag electrode with a Rh-coated AFM tip grounded.

5: *I-V* characteristics of a cross-point structured Ag/TBAP/Pt device:

As stable resistive switching and quantized conductance in the TBAP film were observed, we also fabricated a cross-point structured Ag/TBAP/Pt device and examined its resistive switching behaviour. The device was fabricated on a SiO_2/Si substrate and had a junction area of 50 × 50 μm^2. A spin coated TBAP film with a thickness of ~20 nm was sandwiched between the bottom Pt and top Ag electrodes. An optical image of the fabricated Ag/TBAP/Pt device is shown in the inset of Figure S5.

The *I-V* measurements were performed on Ag/TBAP/Pt devices under vacuum conditions (10^{-4} Pa) using a two-probe system equipped with a semiconductor characterization system (Keithley 4200SCS/F). The bias voltage was applied to the top Ag electrode with a sweep rate of 21 mV s^{-1}, while the bottom Pt electrode was grounded. Figure S5 shows the typical *I-V* curves obtained for consecutive 8 sweep cycles, including the forming process and subsequent switching cycles. The one-sided arrows indicate the direction of the current conducted through the device. Under the forward bias, the device exhibited a SET operation from the OFF state to the ON state, resulting in the formation of metal filaments. When the bias was reversed, the device exhibited a RESET operation from the ON state to the OFF state, which corresponds to the dissolution of metal filaments formed.

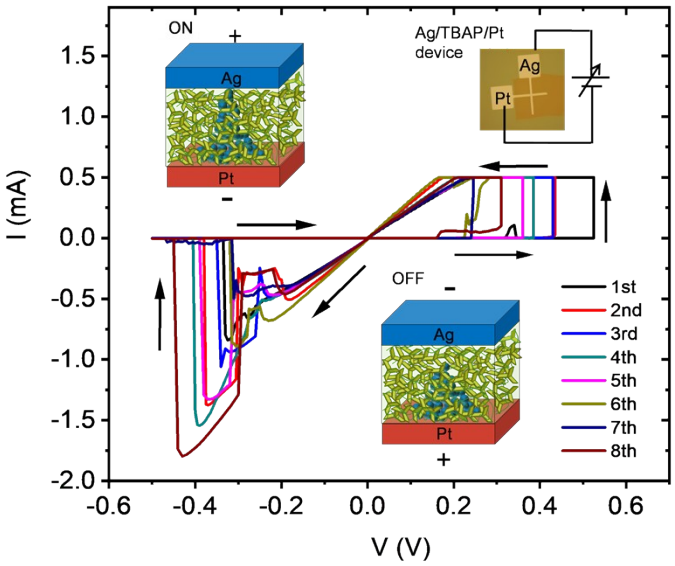

Figure S5: Typical *I-V* curves obtained for an Ag/TBAP/Pt device. The insets at the right-upper side depict an optical image of the fabricated device on an SiO_2/Si substrate. The insets at the left-upper and right-lower sides show the schematic illustration of the ON and OFF states in the Ag/TBAP/Pt device after SET and RESET operation, respectively.

The forming voltage was 0.52 V, as shown by the black *I-V* curve. After the forming process, subsequent resistive switching was obtained under repeated voltage sweeping. The subsequent cycles result in smaller voltages for the SET operation, compared to the forming voltage. The SET and RESET voltages are plotted as a function of the number of sweep cycles, which is shown in Figure S6. The SET voltage ranged from 0.25 V to 0.4 V. Because some parts of the filament remained inside the TBAP matrix after the forming process, the resistive switching occurs in a small gap of the filament, giving rise to smaller SET voltages. The ON state remained when the bias voltage crossed 0 V, and the current increased in magnitude under reverse bias, indicating nonvolatile switching. The current decreased somewhat around -0.25 V but increased again with further negative voltage sweeping. Finally, the device was RESET in a voltages range between -0.3 V to -0.45 V. Although the SET and RESET voltages varied to some extent in cycle-to-cycle, the device exhibited repeated switching with high OFF/ON resistance ratios of 10^6. The ON-state resistance was maintained to ~500 Ω in cycle-to-cycle. The origin of the current reduction around -0.25 V is not clear. Further investigation is needed to elucidate the observed RESET behavior.

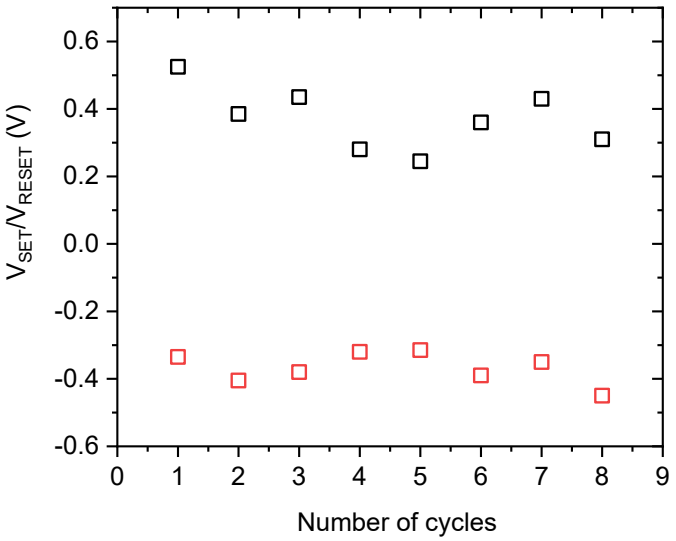

Figure S6: SET and RESET voltages plotted as a function of the number of sweep cycles, which are extracted from the *I-V* curves in Figure S5.

The insets of Figure S5 show schematics of the ON and OFF states in the Ag/TBAP/Pt device. When a positive bias voltage is applied to the Ag electrode, Ag atoms are oxidized to Ag ions at the Ag/TBAP interface, and the Ag ions migrate through the internal free volume (IFV) of the TBAP matrix towards the Pt electrode under the effect of the electric field. When the Ag ions reach the TBAP/Pt interface, nucleation of Ag takes place and Ag filament grows to bridge up between the two electrodes, turning the device ON. When a voltage of opposite polarity is subsequently applied, the Ag atoms are oxidized in the filament and dissolved into the TBAP matrix. Consequently, the filament is ruptured, turning the device OFF. We anticipate that the interlocking TBAP matrix having IFV might help in the migration of Ag atoms during the formation and dissolution of metal filaments.

It is to be noted that a current compliance function of the semiconductor characterization system was used instead of a 10 kΩ resistor, and the compliance level of 0.5 mA was required to realize repeatable switching. This higher current compliance causes an abrupt jump in the current during the SET operation. Therefore, quantized conductance states in a range of $1G_0 - 10G_0$ were not observed, which are different from the C-AFM measurements. Moreover, the formation of multiple filaments cannot be excluded during the SET operation, because of the large junction area. The switching characteristics can be improved by optimizing the device structure such as film thickness and junction area, but we cannot draw any conclusion at this stage. Further investigation is also required for understanding the operating mechanism and optimizing the material and device parameters.

References

1. Park, T. H., Song, S. J., Kim, H. J., Kim, S. G., Chung, S., Kim, B. Y., ... & Hwang, C. S. (2015). Thickness effect of ultra-thin Ta_2O_5 resistance switching layer in 28 nm-diameter memory cell. *Sci. Rep.*, *5*(1), 1-9.

2. Mohapatra, A. R., Tsuruoka T., Krishnan K., Hasegawa T., & Aono M. (2015). Effects of temperature and ambient pressure on the resistive switching behaviour of polymer-based atomic switches. *J. Mater. Chem. C*, *3*(22), 5715-5720.

3. Krishnan, K., Gubicza, A., Aono, M., Terabe, K., Valov, I., & Tsuruoka, T. (2021). Impact of moisture absorption on the resistive switching characteristics of a polyethylene oxide-based atomic switch. *J. Mater. Chem. C*, *9*(34), 11198-11206.