Experimental section

General Procedures. Compounds Tr and TrO\textsubscript{3} were synthesized followed the procedure in our previous report.\textsuperscript{1} Absorption spectra were recorded on a PerkinElmer Lambda 35 UV-vis Spectrometer. Photoluminescent (PL) spectra were carried out on a PerkinElmer LS55 Luminescence Spectrometer. Cyclic voltammetry was performed using BASI Epsilon workstation and measurements were carried out in acetonitrile containing 0.1 M n-Bu\textsubscript{4}NPF\textsubscript{6} as a supporting electrolyte. Carbon electrode was used as a working electrode and a platinum wire as a counter electrode; all potentials were recorded versus Ag/AgCl as the reference electrode. The scan rate was 50 mV·s\textsuperscript{-1}. Optical microscopy was conducted with an Olympus BX-51 microscope. Scanning electron microscopy (SEM) images were obtained with a cold field emission scanning electron microscope (Hitachi S4800) operated at an accelerating voltage of 1.0 kV. Atomic force microscopy (AFM) studies were performed with a Nanoscope IIIa microscope (Extended Multimode, Digital Instruments, Santa Barbara, CA). All experiments were carried out in tapping mode at ambient temperature. Scanning Tunneling Microscopy (STM) studies were performed with a Solver P47 apparatus under ambient conditions. The STM tips were made of electrochemically etched tungsten.
Figure S1. HOMO and LUMO distribution of Tr and TrO₃ calculated by DFT using B3LYP/6-311+G (d, p)//B3LYP/6-31G (d) level. All the hexyl groups were replaced with ethyl groups for simplicity.

Figure S2. AFM height images (a) and cross section (b) of thin film of 1 Tr:TrO₃ (1:1).
Figure S3. Scanning Electron Microscopy (SEM) images of self-assembled (a) Tr; (b) TrO₃ and (c) Tr:TrO₃ in hexane.

Figure S4. I-V characteristics of control devices with the structure ITO/Tr or TrO₃/Al. The results suggest that no current transition from low to high level happen in single component. The numbers on the curves correspond to the scanning order.
Figure S5. $I-V$ characteristics of device with the double-layer structure ITO/TrO$_3$/Tr/Al. The results suggest that similar flash memory effect to device fabricated by Tr:TrO$_3$ (1:1). The number on the curves corresponded to the scanning order.

Figure S6. UV-vis absorption spectra of Tr:TrO$_3$ film by applying a bias of -2.5 V after the film device was turned “On” by a 3 V bias. The CT transition can be erased by such a manner. The time interval is 10 s.
Figure S7. I-V characteristics of single wires of (a) Tr and (b) TrO$_3$ under dark and illumination.