

Proton-Triggered Switch Based on Molecular Transistor with Edge-on Gate

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1. Preparation of self-assembled monolayers (SAMs)

Prior to each experiment, the substrate was briefly annealed in a propane flame. The self-assembled monolayers (SAMs) of the five molecules were prepared in a single step using tetrabutylammonium fluoride (TBAF) as the deprotecting agent under a N₂ protected environment in a tetrahydrofuran (THF) solution containing ca. 5×10^{-5} M of the target molecule. A gold substrate prepared using the procedure described above was immersed in the solution for 12 hours. For the measurement of the unprotonated samples, the substrate was then washed successively with THF and ethanol, dried under a stream of N₂, and immediately used for experiment. For the measurement of the protonated samples, the substrate was further submerged in a solution of trifluoroacetic acid (TFA) 100 mM in THF for 15 min, subsequently washed with THF and then dried under a stream of N₂, and immediately used for experiment. For the measurement of the deprotonated samples, the protonated substrate was washed with THF and distilled water, and then was further submerged in 100 mM Na₂CO₃ water/acetonitrile (v/v, 5/5) solution for 15 min, subsequently washed with water, THF and then dried under a stream of N₂, and immediately used for experiment.

2. Break-junction experiment for single molecule junctions

The STM-BJ experiments were performed with a previously described STM break-junction setup. Briefly, fresh gold tips were prepared by mechanically cutting a 0.25 mm gold wire (99.998% Alfa Aesar). The experiments were carried out in degassed toluene ($\geq 99.9\%$ Sigma-Aldrich), which reduced possible surface contamination. Before use, the STM Teflon solvent holder was sonicated in acetone and dried with N₂. During measurement, the solvent holder was placed over the gold-SAM surface and filled with a couple drops of toluene. A typical break-junction experiment comprised thousands of current-distance traces. Of these traces, $\sim 30\%$ (300 \sim 500 effective curves) displayed plateaus that corresponded to the formation of a molecular bridge and were employed to build the histograms. The break-junction experiments were performed at a bias

of 100 mV.

3. *I-V* recording for single molecule junctions

The *I-V* recording experiments were carried out at 100 mV of bias voltage in toluene. Positive bias means that the substrate is positive and the tip negative. The entire process consists of iterations of three steps, tapping, conductance step detection and *I-V* recording, which is in contrast to the single-step tapping procedure used in the STM break junction measurements. In the tapping step, the tip is moved towards the substrate until the current reaches a preset threshold, and then is retracted until it reaches a lower preset current. In the present method, the conductance step detection is applied during each retraction cycle to identify conductance steps. The measured conductance range was selected according to the previously measured conductance histogram of each molecule. Once a conductance step is detected, the *I-V* recording step is activated, which involves the following sub-steps: 1) The tip is immediately held in position, 2) the current -voltage curve was recorded from + 1.5 V to – 1.5 V quickly (10 Hz), 3) upon completion of the *I-V* curve, the tip was pulled away from the substrate until the current drop to a preset value, and the measurement started over again. For the data selection, *I-V* curves that are incomplete or contain large switching noises are detected and removed from statistical analysis. This procedure allowed us to obtain complete *I-V* curves for statistical analysis.

Energy offsets φ_0 and voltage division factor γ of the molecular junctions are calculated following the work by Baldea, with the equation: ¹

$$\varphi_0 = 2 \frac{e|V_{t+} V_{t-}|}{\sqrt{V_{t+}^2 + 10|V_{t+} V_{t-}|/3 + V_{t-}^2}} \quad (1)$$

$$\gamma = -\frac{1}{2} \frac{V_{t+} + V_{t-}}{\sqrt{V_{t+}^2 + 10|V_{t+} V_{t-}|/3 + V_{t-}^2}} \quad (2)$$

4. Other characterization

The contact angle measurements were performed using a KSV (Helsinki, Finland) CAM 200 contact angle

goniometer. The X-ray photoelectron spectroscopy (XPS) measurements were conducted on an ESCALAB-250 spectrometer using a monochromatic Al K α (1486.6 eV) as radiation source. The ultraviolet absorption spectra were recorded by a UV-vis spectrometer, and the scan range was set from 300 nm to 500 nm. ^1H nuclear magnetic resonance (^1H NMR) spectra were recorded on a Bruker AV400 spectrometer by using deuterated chloroform (CDCl_3) as solvent and tetramethylsilane (TMS) as an internal standard. For the protonation/deprotonation cycle measurement: 1) ~ 4 mg of PPC-Cl sample was first dissolved in 1 mL of CDCl_3 for the ^1H NMR measurement; 2) the solution was further added ~ 15 μL of TFA/AA for the ^1H NMR measurement; 3) the solution was further added an excess of anhydrous Na_2CO_3 powder and stirred for 10 min, after filtrated with a 220 nm PVDF filter to remove the inorganic salt, the clear solution was used for the ^1H NMR measurement; 4) steps 2 and 3 were repeated one more time to finish the whole cycle measurement.

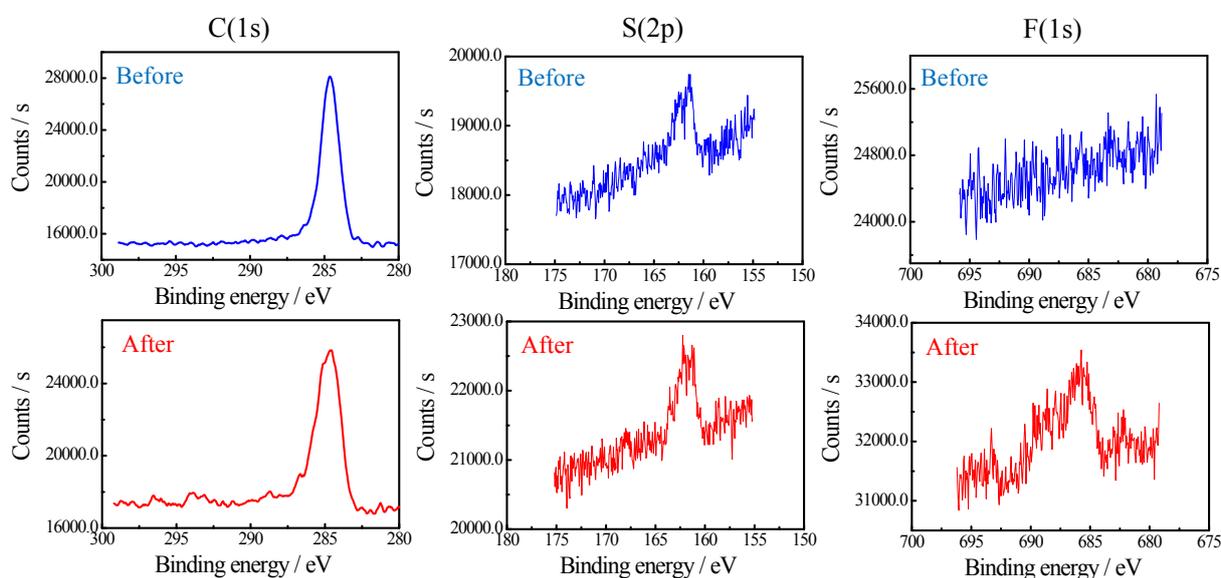


Figure S1 | XPS characterization of elements C, S and F of PPC-OCH $_3$ self-assembled monolayer before and after treated with TFA.

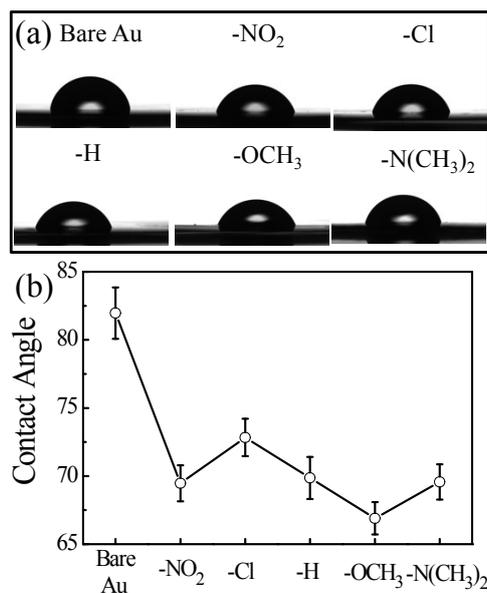


Figure S2 | (a) Photographs of water droplets on the PPC-based self-assembled monolayers (SAMs). (b) Statistical average values of the contact angle of the PPC-based self-assembled monolayers (SAMs), where 3 individual measurements was carried out to extract the average contact angle.

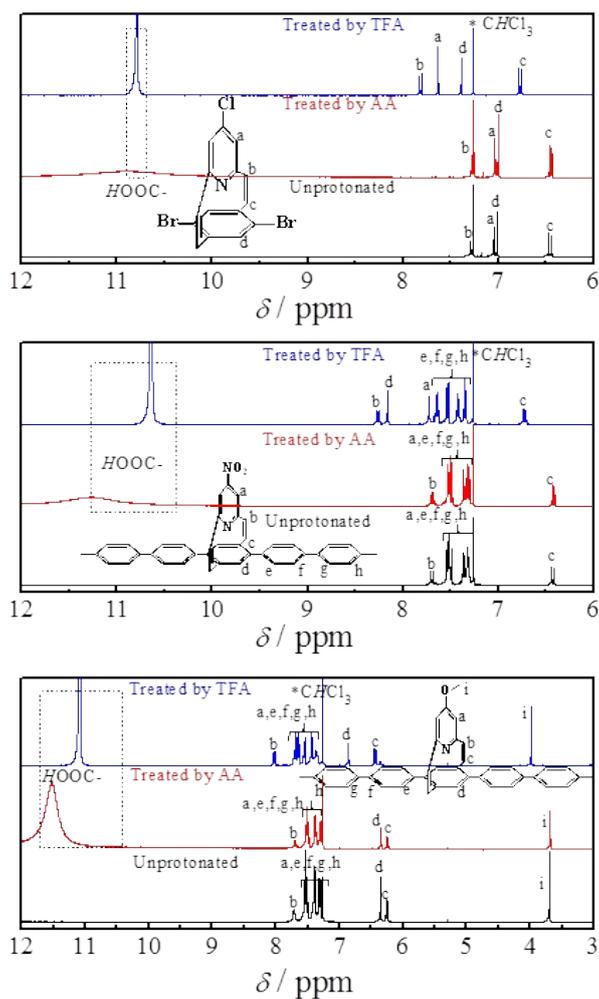


Figure S3 | ¹H-NMR spectra of the PPC-based molecules treated by TFA and AA

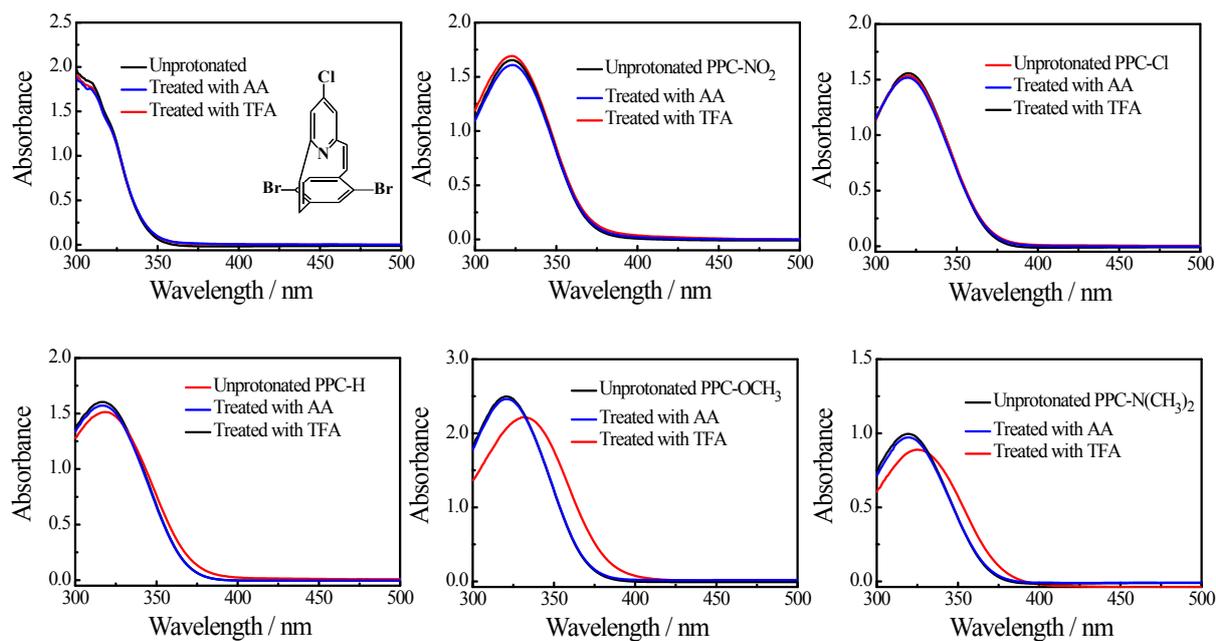


Figure S4 | UV-vis spectra of the PPC-based molecules treated by TFA and AA.

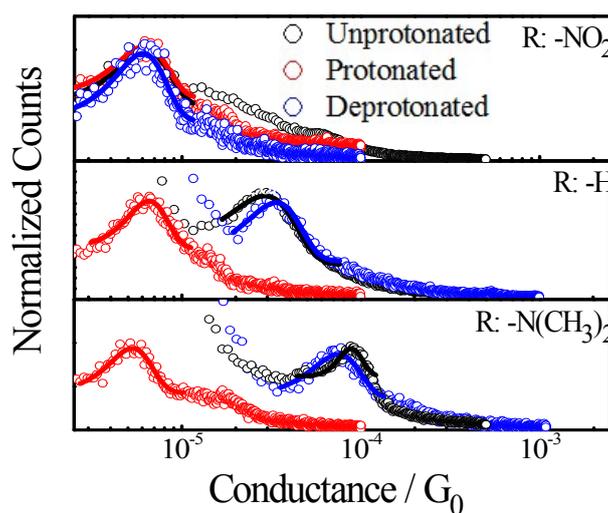


Figure S5 | Conductance histograms of the unprotonated, protonated and deprotonated molecular wires with different substituents (R): $-\text{NO}_2$, $-\text{H}$, and $-\text{N}(\text{CH}_3)_2$.

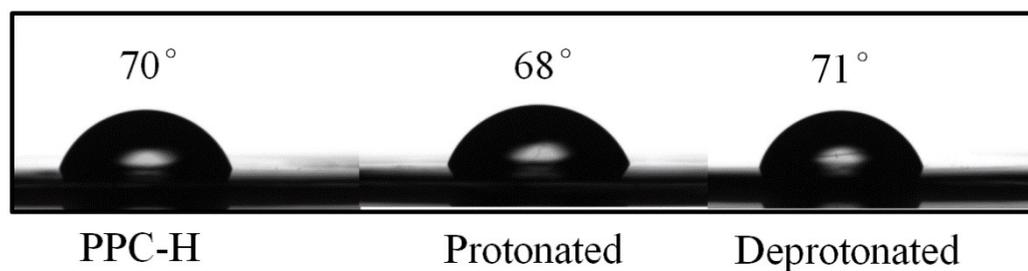


Figure S6 | Photographs of water droplets on the PPC-H self-assembled monolayers (SAMs).

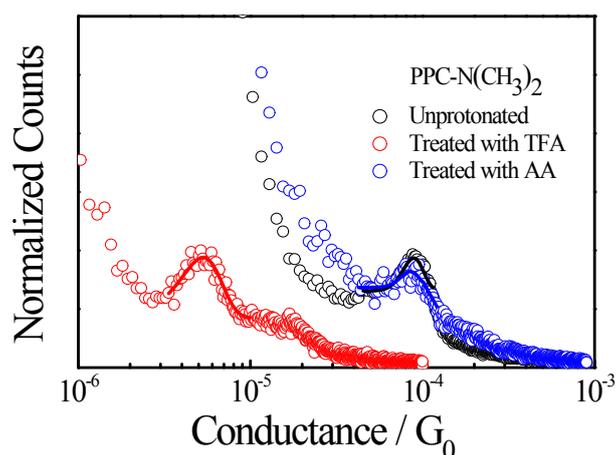


Figure S7 | Conductance histograms of the PPC-N(CH₃)₂ molecules treated with TFA and AA.

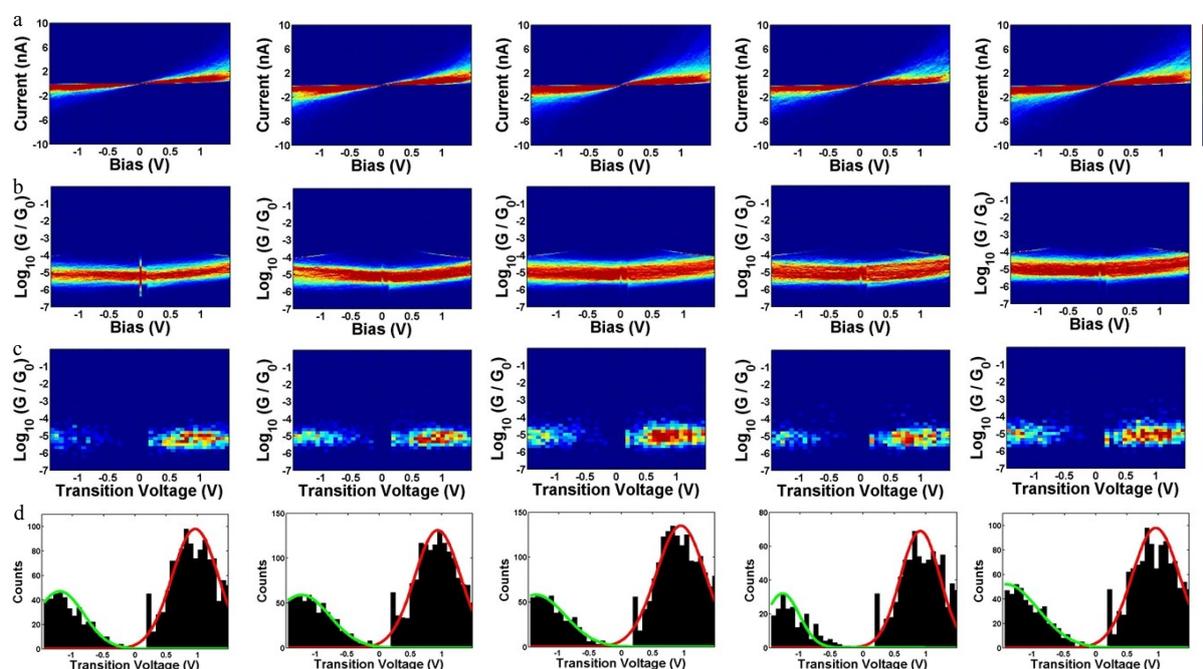


Figure S8 | (a) Current-voltage 2D histograms, (b) conductance-voltage 2D histograms, (c) transition voltage 2D histograms, and (d) transition voltage 1D histograms of the protonated PPC molecular junctions with substituents -NO₂, -Cl, -H, -OMe, -N(Me)₂ (from left to right), respectively.

Table S1 | XPS characterization of PPC-OMe self-assembled monolayers before and after the protonation process.

	Ratio of C/S/F	
	Theoretical	Found
Before	40.0/2.0/0.0	40.0/2.3/0.0
After	42.0/2.0/3.0	42.0/2.7/3.6

Table S2 | Experimental values of $V_{\text{t}\pm}$ for PPC molecular wires and calculated values of φ_0 and γ base on eqs (1) and (2) developed by Baldea.

Molecule	Unprotonated				Protonated			
	$V_{\text{t-}}(\text{V})$	$V_{\text{t+}}(\text{V})$	$\varphi_0(\text{eV})$	γ	$V_{\text{t-}}(\text{V})$	$V_{\text{t+}}(\text{V})$	$\varphi_0(\text{eV})$	γ
PPC-NO ₂	-1.03	1.00	0.87	0.006	-1.20	0.98	0.93	0.043
PPC-Cl	-1.65	1.44	1.33	0.029	-1.25	0.96	0.94	0.056
PPC-H	-1.51	1.36	1.23	0.022	-1.35	0.97	0.98	0.071
PPC-OCH ₃	-1.45	1.25	1.16	0.032	-1.31	0.92	0.93	0.076
PPC-N(CH ₃) ₂	-1.21	1.19	1.03	0.004	-1.38	0.98	0.99	0.073

References

1. Bâldea I *Physical Review B* **2012**, *85*, 035442.