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Electrochemical gating for single-molecule electronics with graphene contacts

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Experimental Details

Synthesis of target 6V6 molecule

The used N,N'-Di-(6-(thioacetyl)hexyl)-4,4'-bipyridinium bis(hexafluorophosphate) (6V6) molecule was synthesized by literature methods.¹ All other reagents were commercially available and used as received. The synthetic route was shown in Figure S1. Nuclear magnetic resonance (NMR) and Quadrupole-Time of Flight mass spectrum (Q-TOF MS) techniques were used to analyze the compound. The ¹H NMR and ¹³C NMR spectra were recorded on a 400 MHz spectrometer.



Figure S1: The synthetic route of used 6V6.

Thioacetic acid S-(6-bromohexyl) Ester (1). A 250 mL round-bottom flask was charged with 50 ml THF. Add 1,6dibromohexane (10.68 g, 43.8 mmol) into flask. An addition funnel containing potassium thioacetate (2.50 g, 21.9 mmol) in THF was attached to the flask, then the whole apparatus was protected by nitrogen. Then potassium thioacetate solution was added to the 1,6-dibromohexane solution at a rate of roughly 1 drop per second. After the addition was complete, the mixture was stirred for 24 h at room temperature ($21^{\circ}C$). During reaction, TLC plate was used to identify the reaction with Rf=hexane: CH₂Cl₂=10:1, while KMnO4 was used as the color developing agent. The ideal reaction is a monosubstitution reaction, the TLC plate showed two product points, the one of more point identified the unexpected disubstituted product. Then the solvent was removed in vacuo. CH₂Cl₂ was added, the org. soln. washed with deionized water. The mixture was then poured into separatory funnel, and the layer were separated. Then the organic phase solution was collected and dried with MgSO₄, and evaporated. The crude product purified by column chromatography (hexane: CH₂Cl₂=10:1) to provided 3.16 g, 13.2 mmol (60.3%). 1H NMR(400 MHz, CDCl3): δ =3.36 (t, J=6.5Hz, 2H); 2.83 (t, J=7.2Hz, 2H); 2.29 (s, 3H), 1.82(m,2H); 1.55(m, 2H); 1.38(m, 4H) ppm.

N-N'-Di-(6-(thioacetyl)hexyl)-4,4'-bipyridinium dibromide (2). A 100 mL round-bottom flask was charged with 15 mL acetonitrile, 1.50 g product 1, and 0.25 g 4,4'-bipyridine. A condenser-west tube was attached to the flask, the whole apparatus was protected by nitrogen. All the mixture was heated with oil bath to reflux for 30 h. After

reaction, cool the mixture to room temperature. Then the mixture was sonicated 10 minutes. Then the mixture was filtered by Buchner funnel to get the crude product. Then washed the crude product with cold diethyl ether (40 mL). Then the crude product was purified by recrystallization form boiling EtOH to provide 0.75 g product in yield 77%. ¹H NMR(400 Hz, methanol-d4): δ =9.37(d, J=7.2Hz, 4H); 8.87(d, J=5.6Hz, 4H); 4.87(t, J=7.2Hz, 4H); 2.77(t, J=7.2Hz, 4H); 2.23(s, 6H), 2.01(m, 4H), 1.37 (m, 4H); 1.17 (m, 8H) ppm.

N, **N'-Di-(6-(thioacetyl)hexyl)-4,4'-bipyridinium bis (hexafluorophosphate) 6V6 (3).** 0.45 g product 2 added into 40 mL DI water. Then added 1.16 g ammonium hexafluorophosphate into the solution. We can observe the forming of white precipitate immediately. Then filtered the mixture to get white crude product. Then washed the crude product with DI water, then dried the product in vacuo to provided 0.436 g final product 6V6 in yield 81.4%. ¹H NMR(400Hz, Acetone-d6), δ =9.47 (d, J=6.8Hz, 4H); 8.86 (d, J=6.4Hz, 4H), 4.99 (t, J=7.6Hz, 4H), 2.85(t, J=4.4Hz,4H); 2.41(s, 6H); 2.22(m, 4H), 1.58-1.46(m, 12H)ppm. ¹³C NMR (100 MHz, Methanol-d4, 4096 times scan): 196.32, 145.65, 129.45, 61.83, 30.87, 29.43, 29.20, 29.02, 27.54, 25.10 ppm. HRMS showed intensity peak at 619.202[M-PF₆]⁺. The relative spectra are shown in Figure S2.



Figure S2: (a) ¹H NMR, (b)¹³C NMR, and (c)HRMS spectrum for synthesized N, N'-Di-(6-(thioacetyl)hexyl)-4,4'bipyridinium bis (hexafluorophosphate).

Preparation of electrodes

To form a molecular junction, gold and graphene substrates were used as the electrode at each end (source electrode in EC-STM system). The gold substrates (10 mm × 10 mm) were purchased from Arrandee, and were annealed under a butane flame to yield Au (111) textured surfaces. Graphene substrates (10 mm × 10 mm) were purchased from the Graphene Supermarket (US) and each substrate consists of a few layers of graphene on top of a nickel substrate.

The used graphene substrate was examined by the Raman spectroscopy as shown in the Figure S3a. There are two major characteristic bands of graphene, one can be assigned to the sp² in-plane vibration of carbon atoms (G peak, 1580 cm⁻¹). Another one called G' peak appears at 2700 cm⁻¹, which is associated to the disorder vibration peaks of graphene. The electron dispersion of multilayer and monolayer graphene is different, which leads to the obvious difference of Raman spectrum. The intensity of G peak is greater than G' peak, indicating that the graphene substrates used in our experiments are a few layers of graphene.²⁻³ The annealed Au (111) surface was characterised by the STM technique as shown in Figure S3b. The observed regular triangle patterns suggest that the (111) gold substrate is high quality for forming molecular junctions.



Figure S3: (a) Ramam spectrum of a typical graphene substrate (laser:532 nm); (b) A STM image of Au(111) substrate (field of view: 200 nm x 200 nm) with clear triangle patterns.

Cyclic voltammetry

Cyclic voltammograms were recorded using 99% 1-butyl-3-methylimidazolium triflate (BMIM-OTf) as the electrolyte, which was dried for 24 h (80 °C) in air and then degassed by bubbling with nitrogen gas. Measurements were carried out in this dried BMIM-OTf with 6V6 (5 mM) solution, a graphene working electrode (1×1 cm²) and gold (111) working electrode (1×1 cm²) respectively. The working electrode is the same as the substrate used in conductance measurements. All voltammetric measurements were carried out at room temperature, using an CHI660E electrochemical workstation. Ag/AgCl electrode was used as a reference electrode, and Pt served as the counter electrode.

XPS measurement of 6V6 molecules on graphene substrate

XPS measurement was performed on a graphene substrate which had been immersed in a 5 mM 6V6 dissolved under 99.5 % methanol solution. The survey scan Figure S4a shows C, O, and F elements. The presence of oxygen can be partly explained by absorbed or adsorbed water vapor due to the exposure of the test sample to the laboratory atmosphere. The F signal can be attributed to the PF6- counter-ion. Narrow scans of the C 1s and O 1s regions are presented in Figure S4b and Figure S4c. For C 1s region, peaks at 284.8 eV and 286.3 eV are ascribed

as C-C and C-O bonds.⁴ The high-resolution O 1s profile at 532.7 eV and 533.7 eV could be attributed to O-C and O=C components.⁴



Figure S4: (a) Survey scan XPS spectrum for 6V6 molecules on graphene substrate; (b) C 1s spectra; (c) O 1s spectra.

Conductance measurements

The gold STM tips were fabricated by the electrochemical etching method reported by Ren in 2004.⁵ Briefly, a gold wire (Tianjing Lucheng Metal, 99.99%) with 0.25 mm diameter was used as the original material, and a mixture of hydrochloric acid and ethanol (the volume ratio 1: 1) was used as etching solution. The etching was carried out at a fixed voltage of 5 V. In order to minimize the effect of faradaic leakage current to the electrolyte solution the gold STM tips were coated by insulating resin to leave only a minimum of the gold tip end exposed.

The STM based non-contact *I*(s) method as reported by Haiss et al.⁶ has been used to obtain the conductance value of Au|6V6|graphene (Au) junctions. The conductance of Au|6V6|Au was measured as a comparison also by the STM *I*(s) technique. For these measurements with gold substrates a self-assembled monolayer (SAM) was formed by placing the gold substrate for just 60 s in a 0.5 mM solution of 6V6 in ethanol. A schematic diagram of the electrochemical cell used for these measurements is shown in Figure S5. This EC-STM deployed a Bruker STM (Multimode 8, USA) with a fluid cell (ECM-2). As seen in the inset of Figure S4, there are four electrodes in the EC-STM set-up, including two working electrodes (STM tip and substrate), a counter Pt electrode, and a Pt quasi-reference electrode. The latter has been calibrated in our setup against Ag/AgCl to give -0.415 V versus this reference scale. This four-electrode bipotentiostat configuration allows independent electrochemical potential control of the electrode potential of the STM tip and substrate, provided that no contact occurs between them. Measurements for both Au|6V6|Au and Au|6V6|graphene systems were carried out in a 5 mM 6V6 solution in the ionic liquid (BMIM-OTf), while the bias voltage applied to the molecular junction was fixed at +0.3 V. Here, the electrochemical gating is considered as the "electrolyte gating" which relies on the formation of electrochemical double layers along the STM tip-substrate axis.



Figure S5: Schematic diagram of the electrochemical STM-based *I*(*s*) technique, the inset shows the four electrodes system with two working electrodes (STM tip and substrate), Pt counter electrode and Pt reference electrode. The counter and reference electrode provide the gate electrode in this four-electrode bipotentiostat setup with independent electrochemical potential control.

Density Functional Theory calculations

Density Functional Theory (DFT) calculations have been used to model the molecular junctions in presence of their counter ions. Following a well-established procedure,⁷⁻⁸ we have used the Fireball code⁹ to optimize the geometry and determine the corresponding electronic structure of the molecule connected to the electrodes. Basis sets of sp^3d^5 numerical orbitals for Au, sp^3 for C, N and S, and s for H have been used for the calculations using cutoff radii (in atomic units) s = 4.5, p = 4.9, d = 4.3 (Au), s = 4.5, p = 4.5 (C), s = 4.2, p = 4.2 (N), s = 3.1, p = 3.9 (S), and s = 4.1 (H).¹⁰ A pyramid of 35 Au atoms, terminating in a single apex, has been used to model the gold tip. We have considered a supercell of 5×5 C atoms in the XY plane for the graphene monolayer, on top of which we have set a molecule of defined length in the z direction, terminated by a connection with the Au pyramidal tip. The whole geometry has been optimized with Fireball until the forces reached a value below 0.05 eV/Å. A formalism taking into account van der Waals interactions has also been considered to determine the molecule–graphene distance.¹¹ In addition, we have placed two PF₆. ions in the neighborhood of the molecule to reproduce the electrostatic environment of the molecular junction. Then, the full charge of the system has been varied, as a way to simulate the gating of the molecule, by adding or removing electrons to the system and recalculating the electronic density of the junction. In a second step, the conductance of these charged molecular junctions has been evaluated using a Keldysh-Green formalism.¹²

The break-off distance and the junction configuration

To further analyze the configuration of molecular junctions, an estimated total break off distance $S_{\text{break-off}}$ can be calculated by the equation¹³:

$s_{tatal} = s_0 + \Delta s$

While S_0 is the distance between the STM tip and substrate at a predetermined set point current (I_0). Δs is the distance from S_0 to the end of the current plateau and is obtained by statistically analyzing 1D histogram of individual current plateau derived from 2D histogram (Figure S6a). S_0 is calculated by the following equation ¹³:

$$s_0 = \frac{ln^{\text{init}}(G_0 \times \frac{V_{bias}}{I_0})}{\frac{dln(I)}{ds}}$$

For the Au/6V6/graphene system under -250 mV electrochemical potential (on potential), S_0 was calculated as 1.2 nm. The Δs was obtained as 0.6 nm (95th percentile break off length) from Figure S6b, and Figure S6c shows the individual plateau characteristic *I*(s) traces. The $S_{break-off}$ is then determined as 1.8 nm. The values obtained here indicate that the bridge is tilted by about 53° at the average break off point, while the tilt at the 95th percentile is 43°. This molecular orientation is likely to be expected provided a sufficient molecular density on the surface, similarly to the alkanedithiol brush used for similar studies. For Au/6V6/graphene system under 50 mV electrochemical potential (off potential), the s_0 and Δs are found to be 1.1 nm and 0.9 nm from Figure S5e, which gives a value of the $S_{break-off}$ as 2.0 nm. Both calculated break-off distance values are roughly consistent with the 6V6 molecular length (2.46 nm see Figure S7) for fully extended molecule.



Figure S6: a) 2D conductance histogram of Au|6V6|graphene under -250 mV electrode potential, where the white circle indicates the break off region. b) The 1D distance histogram of Δs with the Gaussian fitting line for junctions at -250 mV; c) The selective *I*(s) traces. d) 2D conductance histogram of Au|6V6|graphene under 50 mV electrode potential, where the white circle indicates the break off region. e) The 1D distance histogram of Δs with the Gaussian fitting line for junctions at -250 mV; c) The selective *I*(s) traces. The break off region of Au|6V6|graphene under 50 mV electrode potential, where the white circle indicates the break off region. e) The 1D distance histogram of Δs with the Gaussian fitting line for junctions under 50 mV; f) The selective *I*(s) traces.



Figure S7: The calculated molecular length of 6V6 molecule with its lowest energy configuration, showing a value of 2.46 nm.

Au-6V6-Au conductance measurements

As a reference for the graphene electrode measurements, the conductance of Au|6V6|Au junctions are measured by STM *I*(s) technique in air atmosphere, and EC-STM *I*(s) technique in BMIM-OTf solution. The sketch of Au/6V6/Au junction was shown in Figure S8a. The conductance of Au|6V6|Au under air atmosphere was measured as 2.16 nS. Figure S8b shows the relative 1D conductance histogram. The break off distance of Au|6V6|Au under -225 mV was also calculated as shown in Figure S9. Similar result to the length of 6V6 molecule is found, showing a vertical orientation of fully extended molecular configuration (as indicated in Figure S8a).



Figure S8: (a) Sketch of Au/6V6/Au junction. (b) The 1D conductance histogram of Au/6V6/Au which has been measured under air atmosphere.



Figure S9: a) 2D conductance histogram of Au|6V6|Au system under -225 mV electrochemical potential, b) The 1D distance histogram of Δs for junctions under -225 mV. Inset: the selective *I*(s) trace.

Figure S10a represents the specific 1D conductance histograms of Au|6V6|Au junctions measured in ILs. These conductance histograms were recorded for the marked electrochemical potentials (versus Ag/AgCl). each of the histograms showed a clear peak where the peak position indicated the conductance value of the corresponding molecular junction. The conductance of 6V6 measured in ILs is greater than when it measured in air atmosphere. As show in Figure S10b, we plotted the conductance value obtained for Au|6V6|Au overlapped with its cyclic voltammogram. The plotted conductance data shows a "bell" shape which could prove the effect electrochemical gating. These results are also in good agreement with the results presented by Osorio et al.¹⁴ In the early study, Haiss et al. ¹⁵ have reported the gating effect of Au/6V6/Au junction with aqueous electrolyte which showed the conductance solely increases as overpotential changed from positive to negative. Noted here, the behavior observed using ionic liquid electrolyte is very different from previously reported for aqueous electrolyte. This demonstrates the effectiveness of ionic liquids for single molecule electrolyte gating, presenting a special electrochemical environment for investigations not possible in aqueous electrolytes.



Figure S10:(a) The 1D conductance histograms of Au|6V6|Au junctions. (b) The plot conductance of Au|6V6|Au with error bar against the sample electrochemical potential overlaid with a cyclic voltammogram (blue line) of 6V6 in BMIM-OTf.

Figure S11 illustrates the Au|6V6|Au junction through the isoelectronic Density of States calculation. The electronic density is localized near the redox active part, with no contribution along the alkyl chains.



Figure S11: DFT calculated isoelectronic density of states of the Au|6V6|Au HOMO level, showing the decoupling of the central part with respect to the electrodes, due to the alkyl chains.

Fitting Parameters for Fitting to the Kuznetsov Ulstrup Model

To fit of the Kuznetsov Ulstrup model, we have made small empirical adjustments of the parameters, up and down, which move away from the best fit, but the model remains stable. Table 1 lists the fitting Parameters for fitting to the Kuznetsov Ulstrup Model for ω_{eff} = 1000 cm⁻¹ (for Figure 4).

Table 1. Fitting Parameters for fitting to the Kuznetsov Ulstrup Model for ω_{eff} = 1000 cm⁻¹

Viologen Reduction Peak	First Reduction	Second Reduction
Fraction of the electrode potential	1	1
(ξ) experienced at the redox		
centre.		
Fraction of the bias voltage (γ)	0.5	0.5
electrode potential experienced at		
the redox centre.		
Reorganization energies (λ)	0.27 eV	0.4 eV

REFERENCES

1. B. Ren, G. Picardi, B. Pettinger, *Rev. Sci. Instrum.*, 2004, **75**, 837.

2. J. Wu, H. Xu, J. Zhang, Acta Chim. Sinica, 2014, 3, 301–318.

3. L. M. Malard, M. A. Pimenta, G. Dresselhaus, M. S. Dresselhaus, Phys. Rep., 2009, 473, 51-87.

4. G. Beamson, D. Briggs, *High Resolution XPS of Organic Polymers: The Scienta ESCA300 Database* Wiley, Chichester, 1992.

5. B. Ren, G. Picardi, B. Pettinger, Rev. Sci. Instrum., 2004, 75, 837.

6. W. Haiss, H. van Zalinge, S. J. Higgins, D. Bethell, H. Hobenreich, D. J. Schiffrin, and R. J. Nichols, *J. Am. Chem. Soc.*, 2003, **125**, 15294-15295.

7. Q, Zhang, S. Tao, R. Yi, C. He, C. Zhao, W. Su, A. Smogunov, Y. J. Dappe, R. J. Nichols, and L. Yang, *J. Phys. Chem. Lett.*, 2017, **8**, 5987-5992.

8. Q. Zhang, L. Liu, S. Tao, C. Wang, C. Zhao, C. Gonzalez, Y. J. Dappe, R. J. Nichols, and L. Yang, *Nano Lett.*, 2016, **16**, 6534-6540.

9. J. P. Lewis, P. Jelínek, J. Ortega, A. A. Demkov, D. G. Trabada, B. Haycock, H. Wang, G. Adams, J. K. Tomfohr, E. Abad, H. Wang, and D. A. Drabold, *Phys. Status Solidi B*, 2011, **248**, 1989–2007.

10. M. A. Basanta, Y. J. Dappe, P. Jelínek, and J. Ortega, Comput. Mater. Sci., 2007, 39, 759–766.

11. Y. J. Dappe, J. Ortega, and F. Flores, *Phys. Rev. B*, 2009, **79**, 165409.

12. C. González, E. Abad, Y. J. Dappe, and J. C. Cuevas, Nanotechnology, 2016, 27, 105201.

13. S. Martín, W. Haiss, S. Higgins, P. Cea, M. C. López, R. J. Nichols, J. Am. Chem. Soc., 2012, 112, 3941-3948.

14. H. M. Osorio, S. Catarelli, P. Cea, J. B. G. Gluyas, F. Hartl, S. J. Higgins, E. Leary, P. J. Low, S. Martin, R. J. Nichols,

J. Tory, J. Ulstrup, A. Vezzoli, D. C. Milan, and Q. Zeng, J. Am. Chem. Soc. 2015, 137, 14319-14328.

15. W. Haiss, T. Albrecht, H. Van Zalinge, S. J. Higgins, D. Bethell, H. Höbenreich, D. J. Schiffrin, R. J. Nichols, A. M. Kuznetsov, J. Zhang, Q. Chi, J. Ulstrup, *J. Phys. Chem. B*, 2007, **111**, 6703–6712.