Supporting Information

Enhancing π - π stacking by halogen substituent in Single-Molecule Junction

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Materials and instruments

All available reagents and solvents were obtained from standard chemical suppliers and used without further purification unless mentioned. All reaction were carried out at Argon atmosphere and anhydrous conditions unless otherwise indicated. The column chromatography for purification and concentrated was prepared with 200-300 mesh silica gel.

The NMR spectra were obtained using a Bruker AM-400 MHz or an Ascend-600 MHz instrument. High-resolution mass spectra (HRMS) were recorded on a GCT Premier mass spectrometer using EI-TOF (electron ionization-time of flight), Agilent Technologies 7250 GCQTOF (EI), and Xevo G2 TOF MS (ESI). Single-molecule conductance measurements were carried out using the Xtech scanning tunneling microscope break junction (STMBJ) instrument, and the data were analyzed using XMe open-source code. The UV-vis absorption spectra were recorded on a Shimadzu UV-2600 absorption spectrophotometer.

Experimental Section:

Anthracene derivatives were synthesized according to the reported literature with structural modifications.¹⁻² The final products were fully characterized by H nuclear magnetic resonance (¹H NMR) and mass spectra. Except for the compounds with poor solubility in solution, the other compounds were characterized by ¹³C NMR.

General procedure for the coupling of terminal alkynes to bromoanthracene

To a 100 mL Schlenk tube was charged with bromoanthracene (1.0 equiv.), 4ethynylpyridine hydrochloride (1 equiv. or 2.4 equiv.), PPh₃ (10 mol%), Pd (OAc)₂ (5 mol%), CuI (5mol%), then the tube was degassed and backfilled with Argon 3 times. After that, the Et₃N and toluene were added, the mixture was allowed to stir at 110 °C overnight. The solution was quenched with water, extracted with DCM, dried with MgSO₄. MgSO₄ was filtered and the solvent was evaporated. The residue was purified by column chromatography on silica gel.

4-(anthracen-9-ylethynyl) pyridine (Py-H)



General procedure was followed with 9-bromoanthracene (0.78 mmol, 200 mg, 1.0 equiv.) and 4-ethynylpyridine hydrochloride (0.78 mmol, 109 mg, 1.0 equiv.) and purification by flash column chromatography on silica gel (DCM) afforded **Py-H** as yellow powder (86 mg, 39%);¹H NMR (600 MHz, CDCl₃) δ = 8.71 (d, *J* = 5.0 Hz, 2H), 8.60 (d, *J* = 8.6 Hz, 2H), 8.52 (s, 1H), 8.06 (d, *J* = 8.4 Hz, 2H), 7.66 (m, 4H), 7.56 (m, 2H).

4-((10-bromoanthracen-9-yl)ethynyl)pyridine (Py-Br)



General procedure was followed with 9,10-dibromoanthracene (0.60 mmol, 200 mg, 1.0 equiv.) and 4-ethynylpyridine hydrochloride (0.60 mmol, 84 mg, 1.0 equiv.) and purification by flash column chromatography on silica gel (DCM) afforded **Py-Br** as brown yellow powder (107 mg, 50%); ¹H NMR (600 MHz, CDCl₃) δ = 8.72 (d, *J* = 5.9 Hz, 2H), 8.65 (m, 4H), 7.69 (m, 4H), 7.63 (d, *J* = 5.9 Hz, 2H).

9,10-bis(pyridin-4-ylethynyl)anthracene (Py-Py)



General procedure was followed with 9,10-dibromoanthracene (0.60 mmol, 200 mg, 1.0 equiv.) and 4-ethynylpyridine hydrochloride (1.44 mmol, 200 mg, 2.4 equiv.) and purification by flash column chromatography on silica gel (DCM) afforded **Py-Py** as orange powder (98 mg, 43%); ¹H NMR (400 MHz, CDCl₃) δ = 8.74 (d, *J* = 5.7 Hz, 4H), 8.67 (m, 4H), 7.72 (m, 4H), 7.65 (d, *J* = 5.8 Hz, 4H).

4-(anthracen-2-ylethynyl)pyridine (2-Py-H)



General procedure was followed with 2-bromoanthracene (0.78 mmol, 200 mg, 1.0 equiv.) and 4-ethynylpyridine hydrochloride (0.78 mmol, 109 mg, 1.0 equiv.) and purification by flash column chromatography on silica gel (PE:DCM=3:1) afforded **2-Py-H** as brown yellow powder (86 mg, 40%); ¹H NMR (400 MHz, CDCl₃) δ = 8.65 (d, J = 4.1 Hz, 2H), 8.43 (d, J = 2.6 Hz, 2H), 8.28 (s, 1H), 8.04 (m, 3H), 7.54 (m, 3H), 7.46 $(d, J = 5.6 \text{ Hz}, 2\text{H}); {}^{13}\text{C}$ NMR (150 MHz, CDCl₃) δ = 149.8, 132.9, 132.5, 132.2, 131.5, 130.8, 128.6, 128.3, 128.2, 127.2, 126.7, 126.4, 126.2, 126.0, 125.6, 118.8, 94.7, 87.5; HRMS(EI): [M]⁺ Calcd for C₂₁H₁₃N: 279.1048; found: 279.1051.

4-((6-bromoanthracen-2-yl)ethynyl)pyridine (2-Py-Br)



General procedure was followed with 2,6-dibromoanthracene (0.60 mmol, 200 mg, 1.0 equiv.) and 4-ethynylpyridine hydrochloride (0.60 mmol, 84 mg, 1.0 equiv.) and purification by flash column chromatography on silica gel (PE:DCM=3:1) afforded **2-Py-Br** as brown yellow powder (100 mg, 47%); ¹H NMR (400 MHz, CDCl₃) δ = 8.65 (d, *J* = 2.5 Hz, 2H), 8.40 (s, 1H), 8.32 (s, 1H), 8.25 (s, 1H), 8.19 (s, 1H), 8.01 (d, *J* = 8.8 Hz, 1H), 7.91 (d, *J* = 9.0 Hz, 1H), 7.56 (dd, *J* = 8.9 Hz, 1.6 Hz, 2H), 7.46 (d, *J* = 5.3 Hz, 2H); ¹³C NMR (150 MHz, CDCl₃) δ = 149.9, 133.1, 132.8, 131.4, 131.4, 131.0, 130.3, 130.0, 129.9, 129.5, 128.5, 127.9, 127.0, 125.6, 125.5, 120.4, 119.3, 94.4, 87.8; HRMS(EI): [M]⁺ Calcd for C₂₁H₁₂BrN: 357.0153; found: 357.0150.

9-bromo-10-fluoroanthracene



9,10-dibromoanthracene (500 mg, 1.49 mmol) was dissolved in anhydrous THF (30 mL). The solution was cooled to -78°C using low-temperature reactor. n-Butyl lithium (1.6 M, 1.3 mL, 1.93 mmol) was added to the solution and stirred for 20 minutes. N-fluorobenzenesulfonimide (704 mg, 2.23 mmol) was added at -78°C and the reaction mixture was stirred overnight slowly warming to room temperature. The reaction was quenched with water and the crude product was extracted using EA. The crude product was purified using column chromatography with PE. This yielded light yellow powder (307 mg, 75%).¹H NMR (400 MHz, CDCl₃) δ = 8.52 (d, *J* = 8.8 Hz, 2H), 8.31 (d, *J* =

8.6 Hz, 2H), 7.66 (m, 2H), 7.58 (m, 2H).

4-((10-fluoroanthracen-9-yl)ethynyl)pyridine (Py-F)



General procedure was followed with 9-bromo-10-fluoroanthracene (0.73 mmol, 200 mg, 1.0 equiv.) and 4-ethynylpyridine hydrochloride (0.73 mmol, 102 mg, 1.0 equiv.) and purification by flash column chromatography on silica gel (PE: EA=4:1) afforded **Py-F** as yellow powder (120 mg, 55%); ¹H NMR (400 MHz, CDCl₃) δ = 8.71 (d, *J* = 4.8 Hz, 2H), 8.59 (d, *J* = 8.7 Hz, 2H), 8.34 (d, *J* = 8.6 Hz, 2H), 7.69 (t, *J* = 7.0 Hz, 2H), 7.62 (m, 4H); ¹³C NMR (150 MHz, C₂D₂Cl₄) δ = 156.2, 154.5, 150.0, 133.6, 133.6, 131.6, 128.1, 126.4, 126.4, 126.3, 126.3, 125.7, 121.3, 121.2, 119.1, 119.0, 111.5, 111.4, 97.5, 90.5; HRMS(EI): [M]⁺ Calcd for C₂₁H₁₂FN: 297.0954; found: 297.0956.

9-bromo-10-chloroanthracene



A solution prepared by dissolving 9-chloroanthracene (200 mg, 0.94 mmol) in CHCl₃ (10 ml) was combined with a mixture of NBS (435 mg, 2.44 mmol) dissolved in CHCl₃ (10 ml) and CH₃COOH (10 ml). Under ice-bath conditions, the latter mixture was slowly added to the former solution, and the reaction was allowed to proceed at 40°C for 4 hours. After the reaction, KOH aqueous solution was added to neutralize CH3COOH, the crude product was extracted by DCM and purified by PE column chromatography. This yielded light yellow powder (260 mg, 95%). ¹H NMR (400 MHz, CDCl₃) δ = 8.60 (m, 4H), 7.65 (m, 4H).

4-((10-chloroanthracen-9-yl)ethynyl)pyridine (Py-Cl)



General procedure was followed with 9-bromo-10-chloroanthracene (0.69 mmol, 200 mg, 1.0 equiv.) and 4-ethynylpyridine hydrochloride (0.69 mmol, 96 mg, 1.0 equiv.) and purification by flash column chromatography on silica gel (PE: EA=4:1) afforded **Py-Cl** as yellow powder (130 mg, 60%); ¹H NMR (400 MHz, CDCl₃) δ = 8.72 (d, *J* = 5.8 Hz, 2H), 8.66 (m, 2H), 8.60 (m, 2H), 7.70 (m, 4H), 7.62 (dd, *J* = 4.5 Hz, 1.5 Hz, 2H); ¹³C NMR (150 MHz, C₂D₂Cl₄) δ = 150.0, 133.1, 131.6, 131.4, 128.6, 127.7, 127.6, 126.9, 125.7, 125.5, 115.8, 98.8, 90.6; HRMS(EI): [M]⁺ Calcd for C₂₁H₁₂ClN: 313.0658; found: 313.0660.

STMBJ measurements

The single-molecule conductance was measured using a custom-built STMBJ setup that has been described in our group. ³⁻⁴ The STM tip was freshly cut and flamed from a gold wire (0.25 mm diameter, 99.99%), which were burned to be bead and attached to the piezo. The gold was evaporated on a silicon wafer to fabricate the substrate, which was placed below the tips. In the STMBJ measurement, the gold tip is firstly controlled by a stepper motor to get to the approximate position to contact the substrate, thereafter the tip is controlled by a piezo stack with the approach/retract at the speed of 10 nm/s. During the measurements, 3 µL of 1 mM target molecule in 1,2,4trichlorobenzene (TCB) was prepared and dropped onto the substrate in situ. As a result, the single-molecule junctions can be established and broken repeatedly. The current was used as the feedback signal to control the movement of the gold tip. During the repeated opening and closing cycles, the conductance versus displacement traces were collected, and the traces from the opening cycles were used to perform further analyses. The bias was kept at 100 mV and the real-time conductance was recorded using an I-Vconverter with a sampling rate of 20 kHz. The data were analyzed using the XMe opensource code (https://github.com/Pilab-XMU/XMe DataAnalysis).

Table S1. Single molecule conductance values and stretching distances (with 0.5 nm snapback correction) for Py-X (X = H, F, Cl, Br) and Py-Py.

molecule	HC/stretching distance	LC/stretching distance
Ру-Н	10 ^{-3.44} G ₀ /0.81 nm	
Py-F	10 ^{-3.54} G ₀ /0.71 nm	
Py-Cl	10 ^{-3.50} G ₀ /0.71 nm	10 ^{-4.93} G ₀ /0.95 nm
Py-Br	10 ^{-3.52} G ₀ /0.73 nm	10 ^{-4.63} G ₀ /1.31 nm
Py-Py	10 ^{-3.96} G ₀ /1.56 nm	



Fig. S1. The conductance and junction formation probability (JFP) of **Py-Cl** and **Py-Br** were measured at different concentrations in TCB solvent under a bias voltage of 0.1 V. (a) 1D and 2D conductance histograms of **Py-Br** at different concentrations (1 mM, black; 0.1 mM, blue; 0.01 mM, purple). (b) 1D and 2D conductance histograms of **Py-Cl** at different concentrations (1 mM, black; 0.1 m



Fig. S2. Conductance measurements at different solvents of Py-Br. (a) Logarithmically binned 1D conductance histograms at different solvents of Py-Br. (b-c) The typical 2D conductance-displacement histograms at TCB, TD and PC of Py-Br measurement window respectively.



Fig. S3. (a) Single conductance–displacement traces for HC (light purple) and LC states (purple) of the **Py-Br** junction. (b) 2D correlation analysis of the single-molecule conductance traces for

Py-Br.



Fig. S4. Conductance characterization of **2-Py-H** and **2-Py-Br**. (a) Logarithmically binned 1D conductance histograms for **2-Py-H** and **2-Py-Br**. (b-c) The typical 2D conductance-displacement histograms of **2-Py-H** and **2-Py-Br**.

Flicker Noise Analysis

The conductance data used for flicker noise analysis were collected from an approach similar to STM-BJ. When a molecular plateau was detected during the break junction process, the tip stopped moving and remained stationary for 0.2 s, during which the current was recorded at a sampling rate of 100 kHz. A digital band-pass filter of 100 to 1000 Hz was applied to preprocess the experimental data to isolate the effects of low-frequency vibration and high-frequency noise. We removed the parts in the curve, which obviously does not belong to the molecular junction to eliminate their interference, most of which are due to breakdown of the junction before reaching 0.2 s. After that, we performed a discrete Fourier transformation on the data and integrated the amplitude in the range of 100–1000 Hz to obtain the noise power of the trace. For each trace, we normalized the noise power by the averaged conductance of that trace and constructed the 2D histograms of normalized flicker noise power against conductance.



Fig. S5. Two-dimensional histograms of normalized flicker noise power against conductance for **Py-Cl-LCs** ($10^{-4.93}G_0$, Low Conductance state), **Py-Br-LCs** ($10^{-4.63}G_0$, Low Conductance state), and **Py-Py**.



Fig. S6. Two-dimensional histograms of normalized flicker noise power against conductance for Py-H, Py-F, Py-Cl-HCs and Py-Br-HCs.

UV-vis absorption spectra



Fig. S7. Normalized absorption spectra of Py-Br and Py-H (0.1 mM in TCB solution) at different temperatures.



Fig. S8 Absorption spectra of Py-Br (red) and Py-Cl (green) (0.01 mM in TCB solution).

Theoretical calculations

All electronic structures in this work were conducted using the Gaussian 16 suite of the program.⁵ The molecules investigated were fully optimized by the m062x/6-31+G*⁶, including empirical dispersion corrections DFT-D3 method⁷⁻⁸, and were performed using the tight convergence criterion, which was always followed by the calculation of harmonic vibrational modes. To calculate the BE using SIESTA, we employed a counterpoise method to correct for basis set superposition errors that are inherent with the localized orbital basis sets that were employed. In the case of dimers, two monomers were defined as entity A and entity B. The ground state energy for the total system was calculated using SIESTA and was denoted EAB AB, with the DFT parameters defined previously. The energy of each entity was then calculated on a fixed basis, which was achieved through the use of ghost atoms. Hence, the energy of one monomer in the presence of the fixed basis was defined as EAB A and for the other monomer as EAB B. The BE was then calculated using the following equation

BE = EAB AB - EAB A - EAB B

The ESP was calculated using Gaussian 16 at the level of B3LYP/6-311G.

Sample	ΔH(Kcal/mol)
Py-H-π-stacked dimer	-16.1778544
Py-F-π-stacked dimer	-16.45612442
Py-Cl-π-stacked dimer	-18.48957453
Py-Br-π-stacked dimer	-18.76523963

Table S2. Binding energy of Py-H, Py-F, Py-Cl and Py-Br π-stacked dimers.

solvent	ΔH(Kcal/mol)
heptane	-12.5510081
chlorobenzene	-11.74403024

Table S3. Binding energy of **Py-Br-π-stacked dimer** in heptane and chlorobenzene solvents.



Fig. S9. The optimized molecular structures of Py-H, Py-F, Py-Cl, Py-Br and Py-Py.



Fig. S10 Dipole moments of Py-H, Py-F, Py-Cl and Py-Br.



Fig. S11. The frontier molecular orbitals (HOMO/LUMO) electron density distribution of Py-H, Py-F, Py-Cl and Py-Br.



Fig. S12. The optimized molecular π -stacked dimers structures of Py-H, Py-Br-F, Py-Cl and Py-Br.



Fig. S13. The frontier molecular orbitals (HOMO/LUMO/LUMO+1) electron density distribution of **Py-Br** Monomer, **Py-Br**-π-stacked dimer, **Py-Cl** Monomer and **Py-Cl**-π-stacked dimer.

The enhanced intermolecular interaction of π -stacked dimers of **Py-Cl** and **Py-Br** compared to those of **Py-F** and **Py-H** is also related to energy level splitting, as the electronic coupling between the frontier orbitals of the two monomers can be estimated through their splitting into bonding and antibonding combinations.



Fig. S14. (a) Calculated energy level diagram of monomer and π -stacked dimer of **Py-Br**. The splitting of energy levels LUMO and LUMO+1 is indicated by ΔL . (b) Calculated energy level diagram of monomer and π -stacked dimer of **Py-Cl**. The splitting of energy levels LUMO and LUMO+1 is indicated by ΔL .

The geometry optimization and transmission functions of the single-molecule device were calculated using GGA and PBE functional with the NEGF approach in Atomistix Tool Kit (ATK) package.⁹⁻¹⁰ To construct the single-molecule device models, the molecule structures were firstly optimized by Gaussian 16. The optimized molecular structures were then placed between two gold electrodes to construct the single-molecule junction. The initial Au-N bond distance was set at 0.23 nm. The geometries of molecules and the gold clusters are optimized in a gas atmosphere with *k*-points sampling ($2 \times 2 \times 132$) with a force threshold of 0.05 eV/Å. The single- ζ polarized (SZP) basis set was used for Au atoms and the double- ζ polarized (DZP) basis set was used for other atoms, with a real-space grid defined with an equivalent energy cut-off of 75 Hartree. The devices were then fabricated to calculate the transmission coefficient, and the transmission spectra dependent on the energy of molecular orbitals were also obtained.

The transmission coefficient $T \in$ at E_F of the electrodes represents the magnitude and the trends of molecular conductance. Due to the uncertainties of the gold electrode contact configuration, solution environment, and the inherent limitations of DFT calculations, the calculated Fermi level (E_F DFT) often deviates from the experimental value, and thus E_F is usually treated as a free parameter.¹¹⁻¹² The charge transport for pyridyl-anchored molecules was reported to be electron-dominated. Hence, we rationally shift the Fermi level toward LUMO resonance. The dashed line represents the Fermi level at which the calculated molecular conductance trend is qualitatively consistent with the experimental results.



Fig. S15. (a) The optimized device configurations for **Py-H**, **Py-F**, **Py-Cl** and **Py-Br**. (b) Calculated transmission functions for **Py-H** (gray), **Py-F** (cyan), **Py-Cl** (green) and **Py-Br** (red).





Fig. S16. ¹H NMR-spectrum (600 MHz, CDCl₃) of Py-H



Fig. S17. ¹H NMR-spectrum (600 MHz, CDCl₃) of Py-Br



Fig. S18. ¹H NMR-spectrum (400 MHz, CDCl₃) of Py-Py



Fig. S19. ¹H NMR-spectrum (400 MHz, CDCl₃) of 2-Py-H





Fig. S21. EI-MS spectrum of 2-Py-H



Fig. S23. ¹³C NMR-spectrum (150 MHz, CDCl₃) of 2-Py-Br







Fig. S25. ¹H NMR-spectrum (400 MHz, CDCl₃) of 9,10-dibromoanthracene



Fig. S27. ¹³C NMR-spectrum (150 MHz, CDCl₃) of Py-F



Fig. S28. EI-MS spectrum of Py-F



Fig. S29. ¹H NMR-spectrum (400 MHz, CDCl₃) of 9-bromo-10-chloroanthracene



f1 (ppm)

Fig. S31. ¹³C NMR-spectrum (150 MHz, $C_2D_2Cl_4$) of Py-Cl



Fig. S32. EI-MS spectrum of Py-Cl

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