

Supporting Information

Chemistry of 4-[(4-bromophenyl)ethynyl]pyridine at metal surfaces studied by STM

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Contents:

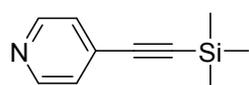
- I. Synthetic Procedures
- II. NMR Spectra
- III. STM related measurement
- IV. Theory calculations for interactions between 4-[(4-bromophenyl)ethynyl]pyridine and various underneath metal surfaces.

I. Synthetic Procedures

Chemicals used in these syntheses were purchased either from Sigma-Aldrich Corporation, Fisher Scientific or Fluorochem Ltd. and used without further purification. Unless otherwise stated, all reactions were carried out under nitrogen or argon with dry solvent, distilled under anhydrous conditions. NMR spectra were recorded in CDCl₃ with a Bruker Avance III spectrometer operating at 400.23 MHz for ¹H spectra and 100.6 MHz for ¹³C spectra. ¹H and ¹³C NMR spectra were referenced relative to TMS ($\delta = 0.00$ ppm) ¹³C NMR spectra were proton-decoupled. C_Q refers to quaternary carbons. Chemical shifts (δ) are reported in ppm and coupling constants in Hz. APCI experiments were carried out on a Bruker micrOTOF-Q III spectrometer interfaced to a Dionex UltiMate 3000 LC or direct insertion probe. Masses were recorded over a range of 100-1600 m/z. EI mass spectra were acquired using a GCT Premier Micromass time of flight mass spectrometer (tof). The instrument was operated in positive mode. Heptacosyl (+) was used as an internal lock mass. Masses were recorded over a range of 100-600 m/z. IR spectra (reported in cm⁻¹) of neat samples were recorded with a Perkin-Elmer Spectrum-One FT-IR spectrometer equipped with a Universal-ATR sampling accessory.

The compounds 4-((trimethylsilyl)ethynyl)pyridine,¹ 4-ethynylpyridine^{1, 2} and 4-((4-bromophenyl)ethynyl)pyridine³ (44BEP) were synthesised according to modified literature procedures. As all compounds have been previously reported in the literature, the synthetic details and spectra presented here are provided solely as confirmation of their synthesis.

Synthesis of 4-((trimethylsilyl)ethynyl)pyridine (**1**)



4-iodopyridine (1 g, 4.88 mmol), Pd(PPh₃)₄ (30 mg, 0.026 mmol) and CuI (14 mg, 0.074 mmol) were added to a round bottom flask (RBF) and degassed by vacuum/Ar cycles. Triethylamine (5 mL) and THF (35 mL) were combined, degassed, and added to the solids *via* cannulation. The mixture was stirred for 15 minutes, following which TMSA (0.81 mL, 5.86 mmol) was added slowly over 15 minutes. A white precipitate was formed. The mixture was left to stir overnight at R.T. The solvents were removed *in vacuo* and the resulting solid was dissolved in CH₂Cl₂ and extracted with H₂O. Chromatography on SiO₂ (hexane:ethyl acetate 10:1 v/v) yielded **1** as a yellow oil.

Yield: 700 mg, 82 %

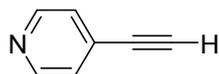
¹H NMR: (400 MHz, CDCl₃) δ = 8.59 (2H, d, *J* = 5.8 Hz), 7.32 (2H, d, *J* = 5.8 Hz), 0.29 (9H, s) ppm.

¹³C NMR: (101 MHz, CDCl₃) δ = 149.7, 131.2, 125.8, 102.0, 100.0, -0.3 ppm.

EI-MS: m/z 175.0811 ([M]⁺) (calc. 175.0817)

IR (ν_{max}/cm⁻¹) 2961, 2166, 1591, 1405, 1249.

Synthesis of 4-ethynylpyridine (2)



4-((trimethylsilyl)ethynyl)pyridine (1) (700 mg, 4.00 mmol) was dissolved in a mixture of MeOH (10 mL) and CH₂Cl₂ (5 mL). KOH (500 mg, 8.91 mmol) was added, and the solution was stirred at R.T. for 4 hours. H₂O (50 mL) was added to the mixture which was then washed with CH₂Cl₂ (3 x 50 mL) and dried over MgSO₄. Chromatography on SiO₂ (CH₂Cl₂:MeOH 100:3 v/v) yielded the product as a light-sensitive white solid.

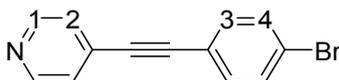
Yield: 155 mg, 38 %.

¹H NMR: (400 MHz, CDCl₃) δ = 8.62 (2H, d, *J* = 6.0 Hz), 7.37 (2H, d, *J* = 6.0 Hz), 3.32 (1H, s) ppm.

¹³C NMR: (101 MHz, CDCl₃) δ = 150.7, 131.3, 127.0, 82.8, 81.9 ppm.

EI-MS: *m/z* 103.0418 ([M]⁺) (calc. 103.0422)

Synthesis of 4-((4-bromophenyl)ethynyl)pyridine (44BEP)



1-bromo-4-iodobenzene (410 mg, 1.45 mmol), 4-ethynylpyridine (150 mg, 1.45 mmol), Pd(PPh₃)₂Cl₂ (7 mg, 0.01 mmol) and CuI (4 mg, 0.02 mmol) were added to an

RBF. Dried and degassed diisopropylamine (3 mL) was added and the solution was stirred under Ar for 3 hours. The solvent was removed *in vacuo*, after which the solid obtained was dissolved in CH₂Cl₂ and washed with aqueous Na₂CO₃. The organic layer was partitioned, dried with MgSO₄ and purified by column chromatography (CH₂Cl₂:MeOH 100:3 v/v) to give an off-white solid.

Yield: 193 mg, 53 %.

¹H NMR: (400 MHz, CDCl₃) δ = 8.64 (2H, d, *J* = 6.0 Hz, H₁), 7.55 (2H, d, *J* = 8.5 Hz, H₄), 7.44 (2H, d, *J* = 8.5 Hz, H₃), 7.41 (2H, d, *J* = 6.0 Hz, H₂) ppm.

¹³C NMR: (101 MHz, CDCl₃) δ = 149.6 (2C, C₁), 133.3 (2C, C₃), 131.9 (2C, C₄), 131.4 (1C, C_Q), 125.6 (2C, C₂), 123.7 (1C, C_{Br}), 121.0 (1C, C_Q), 93.1 (1C, C≡C), 87.6 (1C, C≡C) ppm.

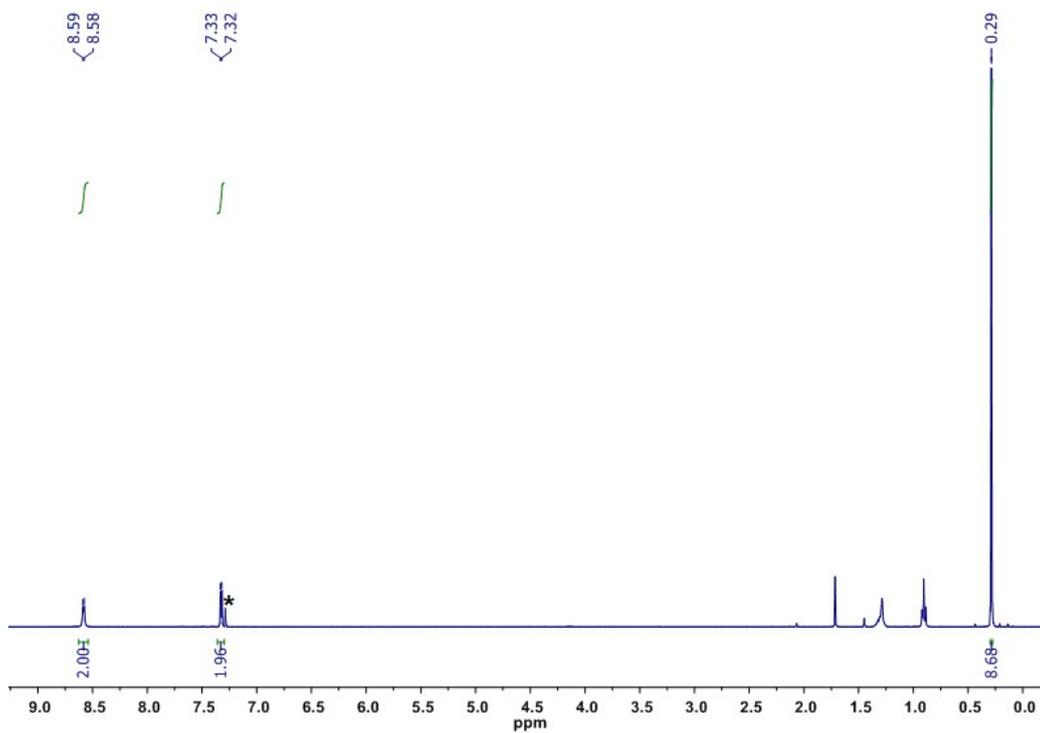
APCI-MS: m/z 257.9916 ([M+H]⁺) (calc. 257.9918)

IR: (ν_{max}/cm⁻¹) 3031, 2218, 1594, 1579, 1539, 1492, 1407, 1218, 1012, 990.

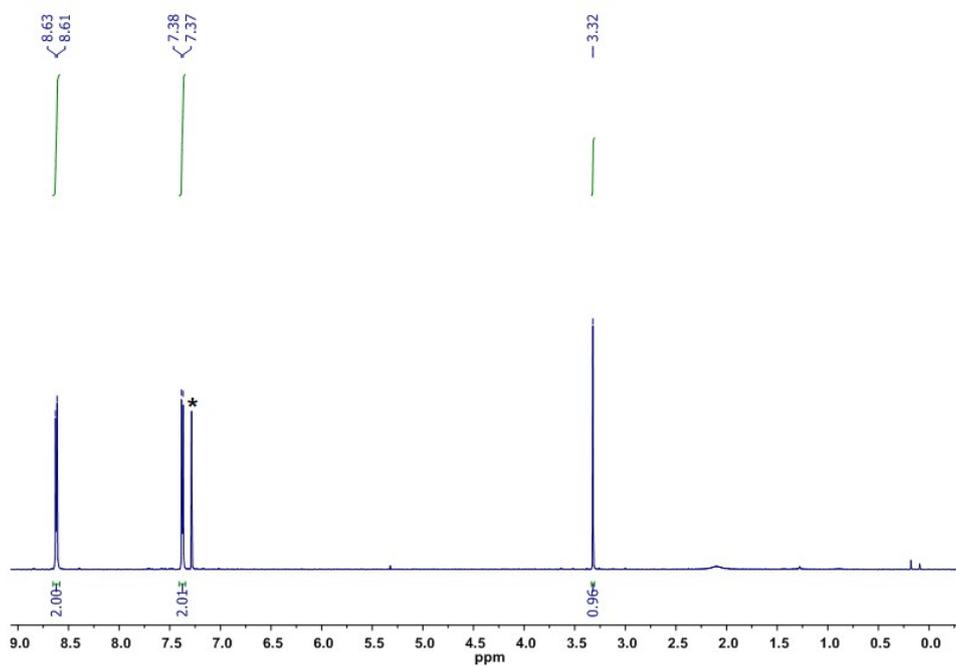
II. NMR Spectra

(* denotes CDCl₃ residual solvent peak)

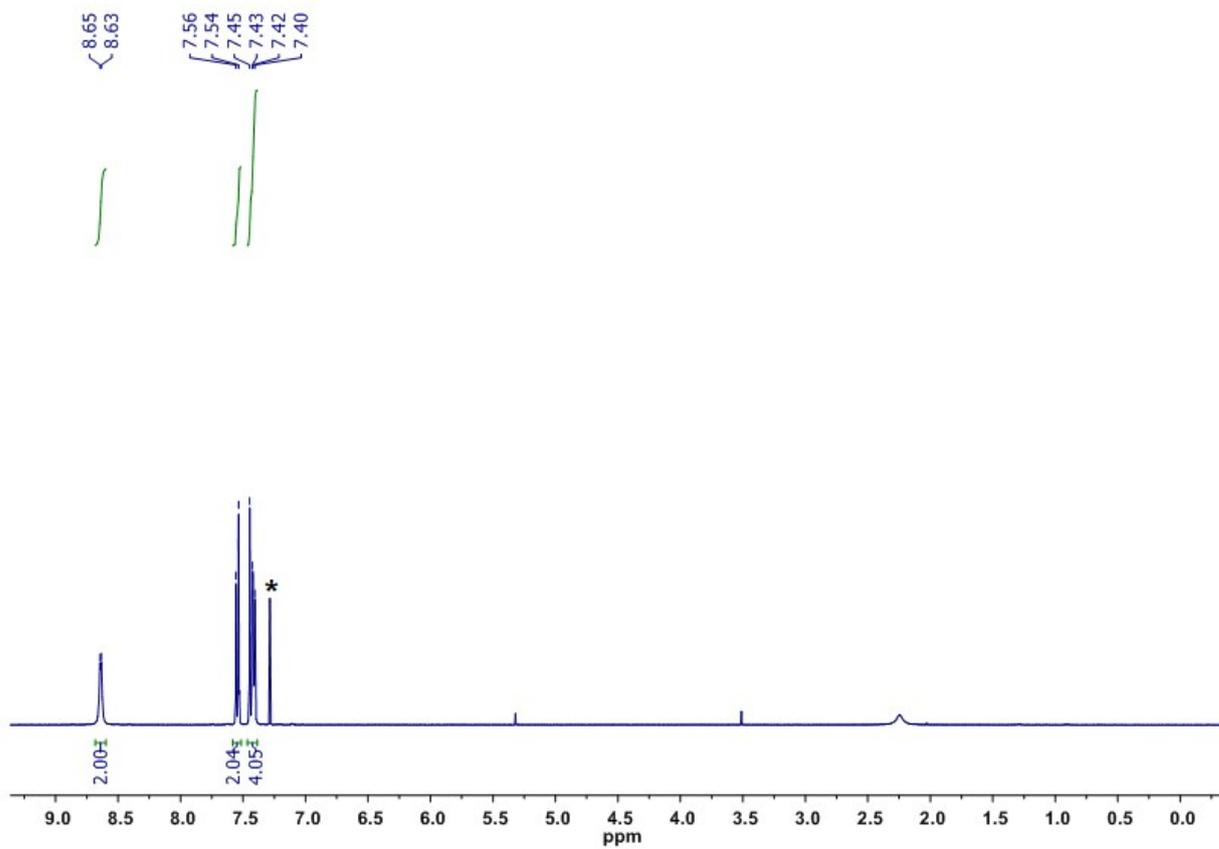
¹H NMR Spectrum of 4-((trimethylsilyl)ethynyl)pyridine (1):



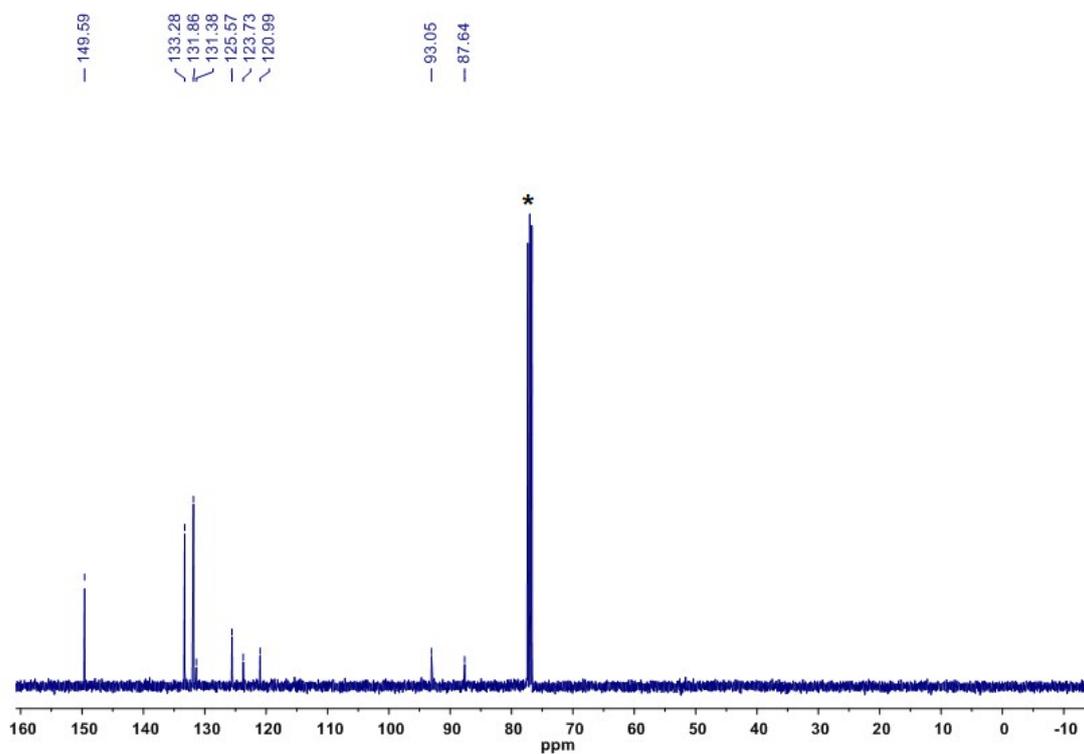
¹H NMR Spectrum of 4-ethynylpyridine (2):



¹H NMR Spectrum of 4-((4-bromophenyl)ethynyl)pyridine (44BEP):

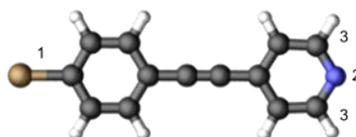


¹³C NMR Spectrum of 4-((4-bromophenyl)ethynyl)pyridine (44BEP):



III. STM related measurements.

The atomically clean crystal surfaces were prepared by several cycles of Ar⁺ sputtering and annealing. All the experiments were performed in an UHV LT-STM system (Createc) operating at T = 77 K. The 44BEP molecules were deposited onto the clean surface and verified by LT-STM before growth. The molecules were deposited in situ at ~300 K using a homemade funnel evaporator. Constant-current STM images were acquired with a tungsten tip.



Scheme S1 Chemical structure of 44BEP and the types of reaction characteristic of the labelled sites: Ullmann reaction Br-C bond (1); N-coordination (2), C-H bond activation (3) Brown, blue, black and white balls represent Br, N, C and H atoms.

IV. Theoretical calculations for interactions between 4-[(4-bromophenyl)ethynyl]pyridine and various metal substrates.

Calculation Method: The density-functional calculations were implemented in the Vienna Ab-initio Simulation Package (VASP)^{4,5} using projector-augmented wave (PAW)⁶ method in conjunction with the Perdew–Burke–Ernzerhof (PBE)⁷ functional. The Grimme-D3 method⁸ was used to describe the van der Waals interaction between 44BEP molecules and metal substrates. A three-layer slab with a (8 × 8) supercell was used to model the metal substrate. The vacuum layer is larger than 15 Å. All the atoms except the bottom metal layer were fully relaxed until the force on each atom was less than 0.01 eVÅ⁻¹. The plane-wave basis was set to an energy cutoff of 400 eV. The Brillouin zone was sampled by Gamma point.

We firstly calculate the binding energy of a single 44BEP molecule on different metal substrates. We tested six different initial molecular positions to determine the most stable binding configurations considering different directions and adsorption sites. Notations can be found in Fig. S1-S4. Binding energy is defined as $E_b = E_{\text{sub}} +$

$E_{44\text{BEP}} - E_{\text{tot}}$, where E_{sub} is the energy of the metal substrate, $E_{44\text{BEP}}$ is the energy of an isolated 44BEP molecule, and E_{tot} is the energy of the combined system. We also check $d_{\text{Br_sub}}$ and $d_{\text{N_sub}}$, the distance between Br and metal substrates, and distance between N and metal substrate, respectively.

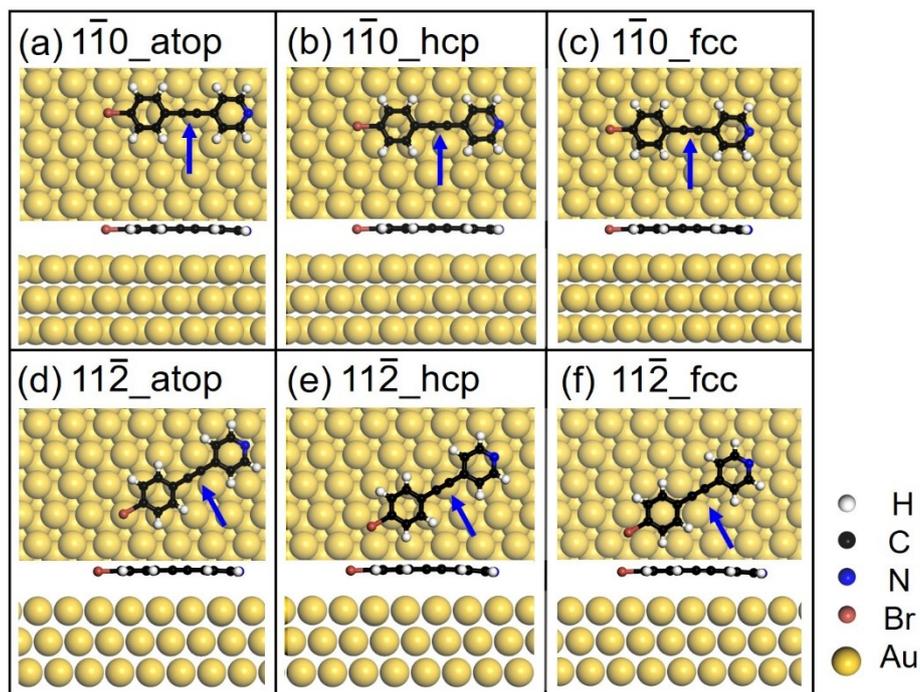


Fig. S1 The top view and side view of six relaxed structures with high-symmetric 44BEP molecular adsorption sites on Au(111) surface. The six structures are distinguished by the adsorption sites of pyridine centre (atop, hcp and fcc) and the direction of the major axis of 44BEP ($[10]$ or $[11]$), which marked on the topside of each structure. The blue arrows indicate the side view direction.

Table S1 Comparison of binding energy E_b and vertical distances $d_{\text{Br}_{\text{sub}}}$ and $d_{\text{N}_{\text{sub}}}$ for six relaxed structures with high-symmetric 44BEP molecular adsorption sites on Au(111) surface.

	10_atop	10_hcp	10_fcc	11_atop	11_hcp	11_fcc
E_b (eV)	1.79	1.82	1.82	1.79	1.85	1.80
$d_{\text{Br}_{\text{sub}}}$ (Å)	3.32	3.28	3.27	3.27	3.29	3.29
$d_{\text{N}_{\text{sub}}}$ (Å)	3.21	3.24	3.24	3.29	3.16	3.16

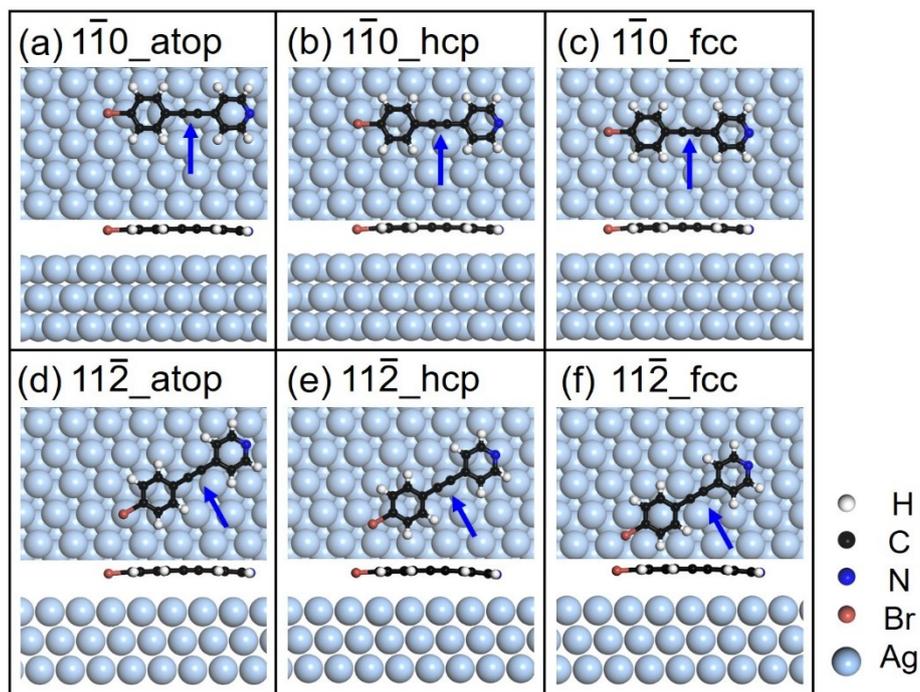


Fig. S2 The top view and side view of six relaxed structures with high-symmetric 44BEP molecular adsorption sites on Ag(111) surface. The six structures are distinguished by the adsorption sites of pyridine centre (atop, hcp and fcc) and the direction of the major axis of 44BEP ([10] or [11]), which marked on the topside of each structure. The blue arrows indicate the side view direction.

Table S2 Comparison of binding energy E_b and vertical distances $d_{\text{Br}_{\text{sub}}}$ and $d_{\text{N}_{\text{sub}}}$ for six relaxed structures with high-symmetric 44BEP molecular adsorption sites on Ag(111) surface.

	10_atop	10_hcp	10_fcc	11_atop	11_hcp	11_fcc
E_b (eV)	1.65	1.69	1.69	1.66	1.72	1.66
$d_{\text{Br}_{\text{sub}}}$ (Å)	3.29	3.20	3.19	3.15	3.25	3.25
$d_{\text{N}_{\text{sub}}}$ (Å)	3.19	3.16	3.18	3.22	3.05	3.11

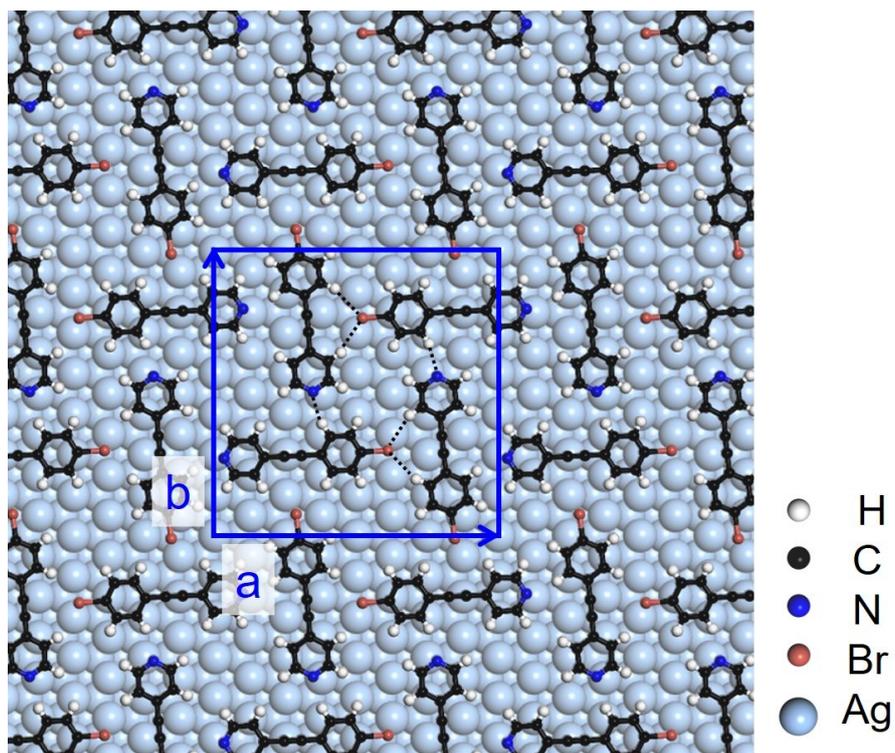


Fig. S3 44BEP molecules self-assembled into a racemic structure by Br...H-C and N...H-C hydrogen bonds on Ag(111) surface. The distances between Br and H of Br...H-C bonds are 0.237 ± 0.002 nm and the distances between N and H of N...H-C bonds are 0.297 ± 0.009 nm. Binding energy is 1.97 eV per molecule.

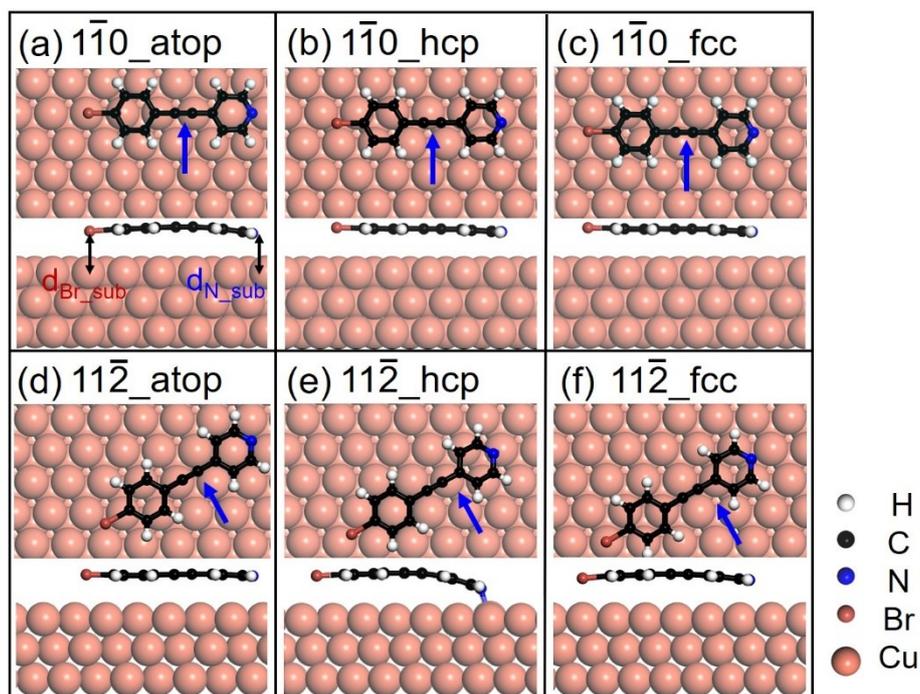


Fig. S4 The top view and side view of six relaxed structures with high-symmetric 44BEP molecular adsorption sites on Cu(111) surface. The six structures are distinguished by the adsorption sites of pyridine centre (atop, hcp and fcc) and the direction of the major axis of 44BEP ([10] or [11]), which marked on the topside of each structure. The blue arrows indicate the side view direction.

Table S3 Comparison of binding energy E_b and vertical distances $d_{\text{Br_sub}}$ and $d_{\text{N_sub}}$ for six relaxed structures with high-symmetric 44BEP molecular adsorption sites on Cu(111) surface.

	10_atop	10_hcp	10_fcc	11_atop	11_hcp	11_fcc
E_b (eV)	1.99	1.97	1.97	1.93	2.08	2.02
$d_{\text{Br_sub}}$ (Å)	2.95	3.24	3.23	3.15	3.14	2.84
$d_{\text{N_sub}}$ (Å)	2.83	2.95	2.95	3.06	2.20	2.78

Table S4 The binding energy (E_b) and vertical distances ($d_{\text{Br_sub}}$ and $d_{\text{N_sub}}$) between the pyridine N and bromine side groups of 44BEP on different substrates.

	Au(111)	Ag(111)	Cu(111)
E_b (eV)	1.85	1.72/1.97	2.08
$d_{\text{Br_sub}}$ (Å)	3.29	3.25/3.26	3.14
$d_{\text{N_sub}}$ (Å)	3.16	3.05/3.21	2.20

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