

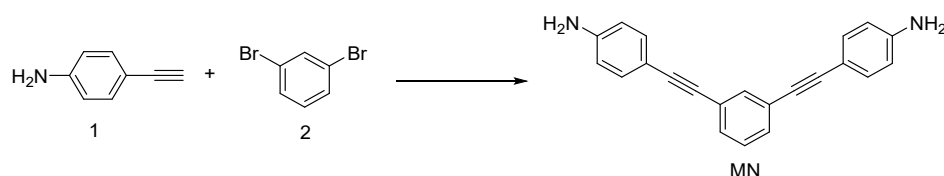
Supporting information

1. Organic synthesis

1.1 General experimental details

All starting materials and reagents used for synthesis are purchased from Aladdin or Macklin or J&K company and used directly. All products were characterised by ^1H and ^{13}C NMR spectroscopy using a Bruker spectrometer. Chemical shifts are reported in parts per million (ppm). The chemical shifts of THF- d_8 is 3.58 ppm and 1.72 ppm in ^1H spectra and 67.21 ppm and 25.31 ppm in ^{13}C spectra. The chemical shifts of CD_3OD is 3.31 ppm in ^1H spectra and 49.00 ppm in ^{13}C spectra. The synthesis of MN, PS, MS, 9 and 11 and was prepared according to the published procedure.¹ The synthesis of 5 were prepared according to the published procedure.²

1.2 Synthesis of 1, 3-Bis (4-aminophenylethynyl) benzene



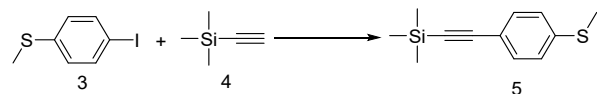
$\text{PdCl}_2(\text{PPh}_3)_2$ (84.8 mg, 0.12 mmol), CuI (18.0 mg, 0.01 mmol), THF (12 mL), and 1,3-dibromobenzene **2** (0.24 mL, 2.0 mmol) were placed in round bottom flask under argon. Then, the solution of 4-ethynylaniline **1** (0.562 g, 4.8 mmol), 0.5 mM aqueous ethanolamine (12 mL) and THF (5 mL) was added in to mixture. The mixture was heated at 60 °C for 26 h. The reaction mixture was cooled to room temperature and diluted with water and EtOAc, filtered under vacuum. The filtrate was extracted with ethyl acetate and washed with water and brine. The organic layer was dried over Na_2SO_4 and evaporated to dryness. The residue was purified by column chromatography (silica gel, dichloromethane/hexane) to afford pale yellow solid.

$^1\text{H-NMR}$ (400 MHz, THF- d_8): δ 7.51 (m, 1H), 7.38 (d, J = 2.76 Hz, 2H), 7.33 (t, J = 4.4 Hz, 1H), 7.26 (d, J = 8.6 Hz, 4H), 6.68 (d, J = 8.6 Hz, 4H), 4.9 (m, 4H).

$^{13}\text{C-NMR}$ (100 Hz, THF- d_8): δ 148.67, 133.00, 132.41, 129.75, 128.22, 124.47,

114.29, 110.83, 90.71, 85.50.

1.3 The synthesis of 1-methylthio-4-[2-(trimethylsilyl) ethynyl] benzene (**5**)

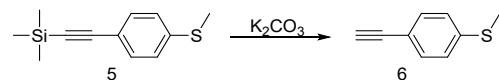


4-iodoanisole **3** (5.00 mL, 20 mmol), PdCl₂(PPh₃)₂ (0.42 g, 0.6 mmol) and CuI (0.14 g, 0.5 mmol) were dissolved in THF (20 mL). After stirring for one hour, the solution of trimethylsilylacetylene **4** (4.15 ml, 30 mmol), diisopropylamine (6 mL) and THF (10mL) were added to mixture and stirred overnight. Next, diluted the reaction mixture with water and ethyl acetate. The mixture was filtered and extract with ethyl acetate. Then the upper organic layer was washed with water and brine. The solution was dried over with Mg₂SO₄ and then evaporated to dryness. The residue was purified by column chromatography (silica gel, hexane) to afford pale yellow oil.

¹H-NMR (400 MHz, CD₃OD): δ 7.39 (d, J= 8.5 Hz, 2H), 7.17 (d, J= 8.6 Hz, 2H), 2.50 (s, 3H), 0.27 (s, 9H).

¹³C-NMR (100 Hz, CD₃OD): δ 139.62, 132.25, 125.65, 119.38, 104.90, 94.17, 15.33, 0.02.

1.1.1. The synthesis of 4-ethynylthioanisole (**6**)

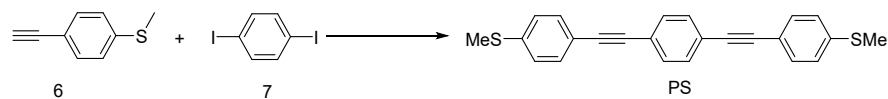


1-methylthio-4-[2-(trimethylsilyl) ethynyl] benzene **5** (1.23 g, 5.58 ml) and potassium carbonate (1.16 g, 8.37 mmol) were dissolved at THF (50 ml). The mixture was stirred for six hours. Then, diluted the mixture with water and extracted with EtOAc, wash with brine. The organic phase was dried over with Mg₂SO₄ and evaporated to dryness. The product **4** was pale yellow liquid. (2.19 g, 100%)

¹H-NMR (400 MHz, CD₃OD): δ 7.39 (d, J= 8.6 Hz, 2H), 7.17 (d, J= 8.6 Hz, 2H), 3.07 (s, 1H), 2.48 (s, 3H).

¹³C-NMR (100 Hz, CD₃OD): δ 140.07, 132.40, 125.73, 118.29, 83.46, 74.09, 15.16.

1.1.2. The synthesis of 1, 4-bis ((4-(methylthio) phenyl) ethynyl) benzene

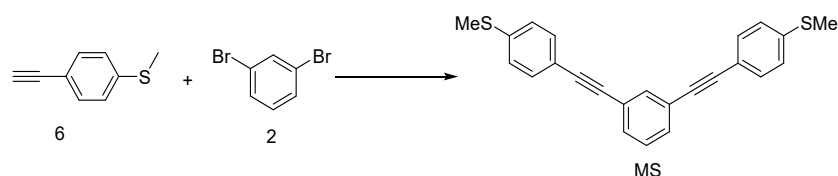


$\text{PdCl}_2(\text{PPh}_3)_2$ (0.084 g, 0.12 mmol), CuI (0.002 g, 0.01 mmol) and 1,4-diodobenzene **7** (0.66 g, 2 mmol) were dissolved in THF (20 mL). After stirring for one hour, the solution of 4-ethynylthioanisole **6** (0.65 g, 4.4 mmol), diisopropylamine (1.32 mL) and THF (10mL) were added and stirred overnight. Then diluted the reaction mixture with water and EtOAc. The mixture was filtered and extract with ethyl acetate. Then the upper organic layer was washed with water and brine. The solution was dried over with Mg_2SO_4 and then evaporated to dryness. The residue was purified by column chromatography (silica gel, dichloromethane/hexane) to afford pale yellow solid.

$^1\text{H-NMR}$ (400 MHz, $\text{THF-}d_8$): δ 7.47 (t, $J=7.8$ Hz, 8H), 7.24 (d, $J=7.8$ Hz, 4H), 2.53 (s, 6H).

$^{13}\text{C-NMR}$ (100 Hz, $\text{THF-}d_8$): δ 143.25, 139.35, 137.54, 135.20, 131.91, 131.49, 128.30, 125.85, 14.17.

1.1.3. The synthesis of 1, 3-bis ((4-(methylthio) phenyl) ethynyl) benzene



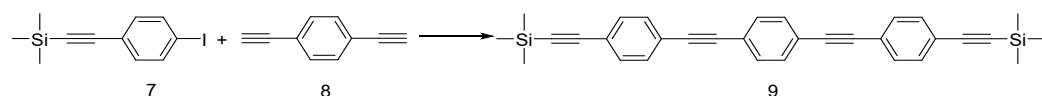
$\text{PdCl}_2(\text{PPh}_3)_2$ (0.098 g, 0.14 mmol), CuI (0.026 g, 0.14 mmol) and 1,3-dibromobenzene **2** (0.57 g, 2.4 mmol) were dissolved in THF (20 mL). After stirring for one hour, the solution of 4-ethynylthioanisole **6** (0.89 g, 6 mmol), diisopropylamine (1.68 mL), and THF (10mL) were added and stirred overnight. Then diluted the reaction mixture with water and EtOAc. The mixture was filtered and extract with ethyl acetate. Then the upper organic layer was washed with water and brine. The solution was dried over with Mg_2SO_4 and then evaporated to dryness. The residue was purified by column chromatography (silica gel, dichloromethane/hexane) to afford pale yellow solid.

$^1\text{H-NMR}$ (400 MHz, $\text{THF-}d_8$): δ 7.71 (s, 1H), 7.50 (s, 4H), 7.46 (d, $J=7.7$ Hz, 2H), 7.35

(t, $J = 7.6$ Hz, 1H), 7.24 (d, $J = 8.3$ Hz, 4H), 2.53 (s, 6H).

$^{13}\text{C-NMR}$ (100 Hz, $\text{THF-}d_6$): δ 139.63, 134.48, 131.93, 131.13, 128.48, 125.90, 123.68, 119.30, 89.91, 88.67, 15.39.

1.4 The synthesis of 1, 4-bis((4-((trimethylsilyl)ethynyl)phenyl)ethynyl)benzene

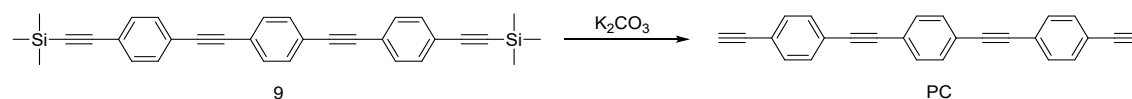


$\text{PdCl}_2(\text{PPh}_3)_2$ (0.18 g, 0.27 mmol), CuI (0.08 g, 0.27 mmol) and ((4-iodophenyl)ethynyl)trimethylsilane **7** (2 g, 2.2 mmol) were dissolved in THF (20 mL). After stirring for one hour, the solution of 1, 4-diethynylbenzene **8** (0.57 g, 4.5 mmol), diisopropylamine (2.8 mL), and THF (10 mL) were added and stirred overnight. Then diluted the reaction mixture with water and EtOAc. The mixture was filtered and extract with ethyl acetate. Then the upper organic layer was washed with water and brine. The solution was dried over with Mg_2SO_4 and then evaporated to dryness. The residue was purified by column chromatography (silica gel, dichloromethane/hexane) to afford pale yellow solid.

$^1\text{H-NMR}$ (400 MHz, $\text{THF-}d_6$): δ 7.52 (s, 4H), 7.48 (d, $J = 8.5$ Hz, 4H), 7.43 (d, $J = 8.3$ Hz, 4H), 0.23 (s, 18H).

$^{13}\text{C-NMR}$ (100 Hz, $\text{THF-}d_6$): δ 133.69, 133.42, 133.25, 133.25, 125.30, 125.09, 106.48, 97.63, 92.63, 92.61, 0.99.

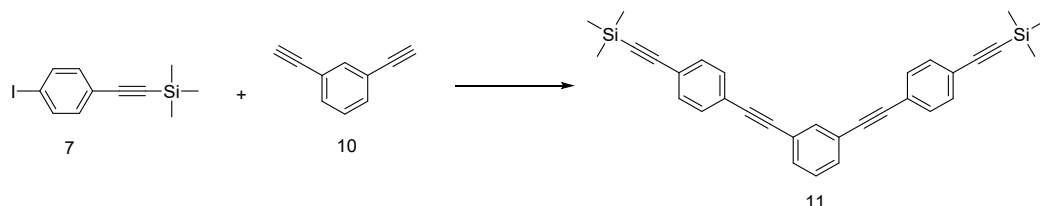
1.5 The synthesis of 1,4-bis((4-ethynylphenyl)ethynyl)benzene



1, 4-bis((4-((trimethylsilyl)ethynyl)phenyl)ethynyl)benzene **9** (0.35 g, 0.74 mmol) and potassium carbonate (0.15 g, 1.12 mmol) were dissolved in THF (20 mL). The mixture was stirred for six hours. Then, diluted the mixture with water and extracted with EtOAc, wash with brine. The organic phase was dried over with Mg_2SO_4 and evaporated to dryness. The product PC was pale yellow liquid. (0.24 g, 100%)

$^1\text{H-NMR}$ (400 MHz, $\text{THF-}d_8$): δ 7.53 (s, 4H), 7.50 (d, $J = 8.6$ Hz, 4H), 7.46 (d, $J = 8.4$ Hz, 4H) 3.70 (s, 2H).

1.6 The synthesis of 1, 3-bis ((4((trimethylsilyl) ethynyl) phenyl) ethynyl) benzene

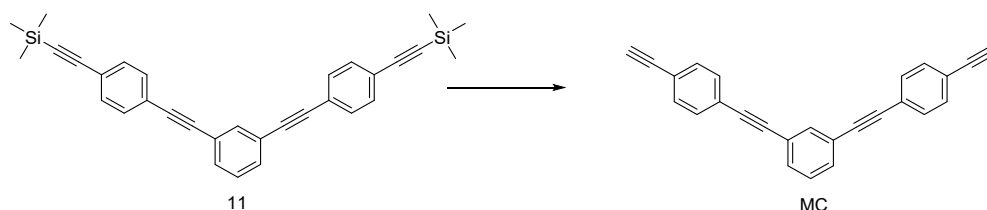


$\text{PdCl}_2(\text{PPh}_3)_2$ (0.18 g, 0.27 mmol), CuI (0.08 g, 0.27 mmol) and ((4-iodophenyl)ethynyl)trimethylsilane **7** (2 g, 2.2 mmol) were dissolved in THF (20 mL). After stirring for one hour, the solution of 1, 3-diethynylbenzene **10** (0.57 g, 4.5 mmol), diisopropylamine (2.8 mL), and THF (10mL) were added and stirred overnight. Then diluted the reaction mixture with water and EtOAc. The mixture was filtered and extract with ethyl acetate. Then the upper organic layer was washed with water and brine. The solution was dried over with Mg_2SO_4 and then evaporated to dryness. The residue was purified by column chromatography (silica gel, dichloromethane/hexane) to afford pale yellow solid.

$^1\text{H-NMR}$ (400 MHz, $\text{THF-}d_8$): δ 7.68 (s, 1H), 7.48 (m, $J = 8.4$ Hz 6H), 7.42 (m, $J = 5.2$ Hz, 4H), 7.38 (d, $J = 7.7$ Hz, 1H), 0.23 (s, 18H).

$^{13}\text{C-NMR}$ (100 Hz, $\text{THF-}d_8$): δ 136.20, 134.21, 133.69, 133.28, 130.67, 125.49, 125.31, 125.05, 106.47, 97.64, 91.99, 91.34, 0.89.

1.7 The synthesis of 1,3-bis((4-ethynylphenyl)ethynyl)benzene



1, 3-bis((4-((trimethylsilyl)ethynyl)phenyl)ethynyl)benzene **11** (0.35 g, 0.74 ml) and potassium carbonate (0.15 g, 1.12 mmol) were dissolved at THF (20 ml). The mixture was stirred for six hours. Then, diluted the mixture with water and extracted with EtOAc, wash with brine. The organic phase was dried over with Mg_2SO_4 and evaporated to

dryness. The product PC was pale yellow liquid. (0.24 g, 100%)

¹H-NMR (400 MHz, THF-*d*₈): δ 7.70 (s, 1H), 7.50-7.46 (m, 8H), 7.39 (t, J=8.2Hz, 1H), 3.69 (s, 2H).

¹³C-NMR (100 Hz, THF-*d*₈): δ 136.17, 133.79, 133.24, 133.21, 130.56, 125.37, 125.08, 124.61, 91.80, 91.13, 84.63, 81.82.

2. UV-vis of target molecules

Both liquid UV-vis and solid UV-vis spectra of target molecules were measured by using Agilent Cary 300 UV-VIS analyser. As shown in Figure S1, the liquid UV of PS in different solvent were studied. When THF was used as solvent, the characteristic peaks indicating the fine structure of benzene can be seen in the spectra. When the solvent is changed, the fine structure of benzene becomes less pronounced due to the polarity of the solvent. When mesitylene was applied as solvent, the fine structure of benzene was disappeared. The maximum absorption bands (λ_{max}) of PS are small shift when different solvent used. It is worth noting that when mesitylene was used as a solvent, the value of λ_{max} is significantly shifted and negative absorption values are observed at wavelength less than 225nm. This is because mesitylene itself has a benzene ring structure and the interaction between it and the target molecule interferes the measurement result. Moreover, considering the solubility of the target molecules in the solvent, we finally chose DCM as the optimum solvent for studied the optical properties of other molecules.

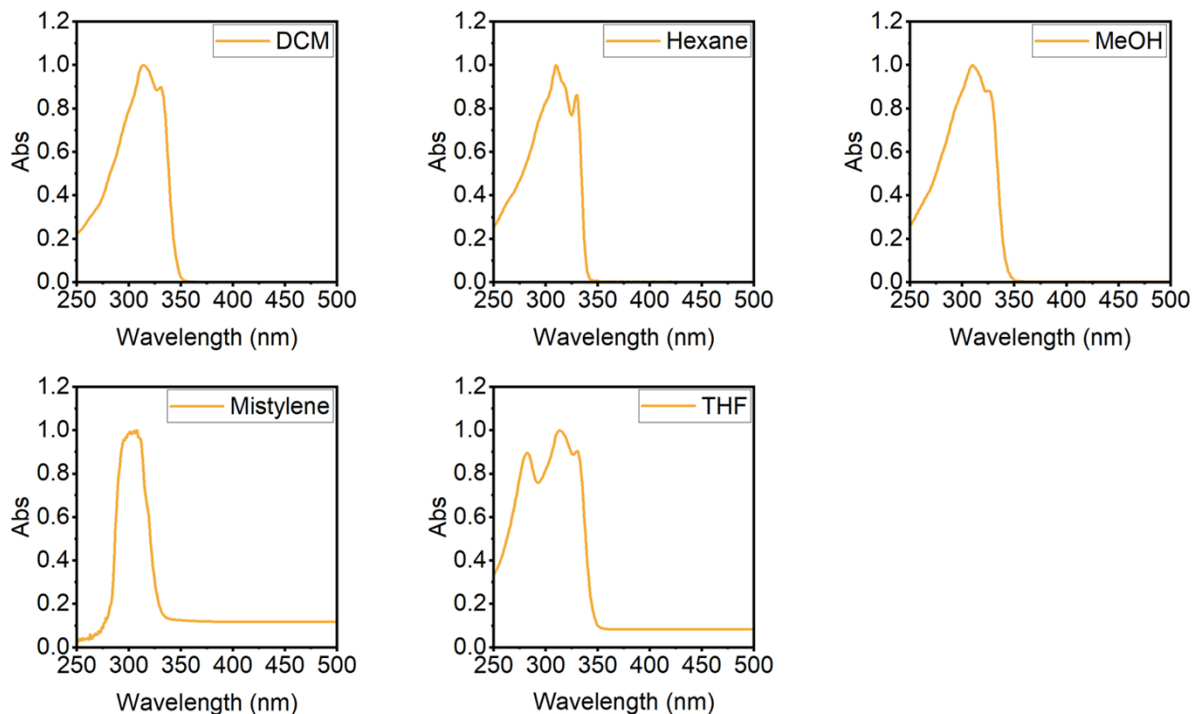


Figure S1 Liquid UV-vis spectra of PS in different solvent

The effect of concentration on λ_{max} was studied by measuring PS in DCM with 0.01mM, 0.02mM, 0.03mM, 0.04mM and 0.05mM concentration. Figure S2 a) and b) shows UV-vis spectra of PS before and after normalisation. It can be clearly seen that normalised spectra of PS with different concentration are overlapping and give the same λ_{max} . This means that the low concentration was not affect the liquid UV-vis results.

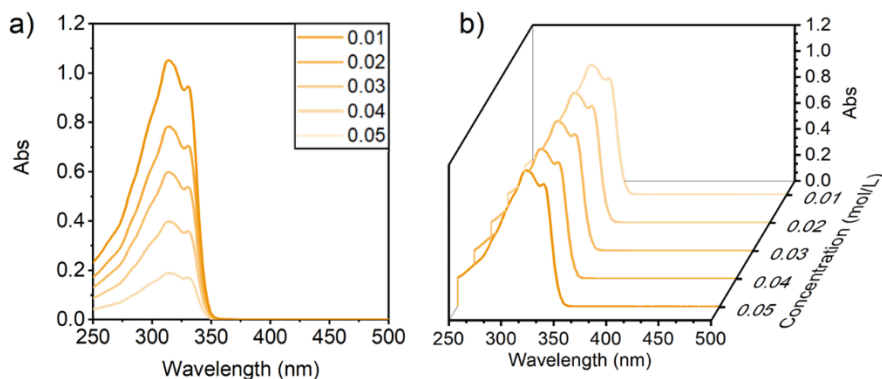


Figure S2 UV-vis spectra of PS before (a)) and after (b)) normalisation

3. 2D conductance-distance histogram

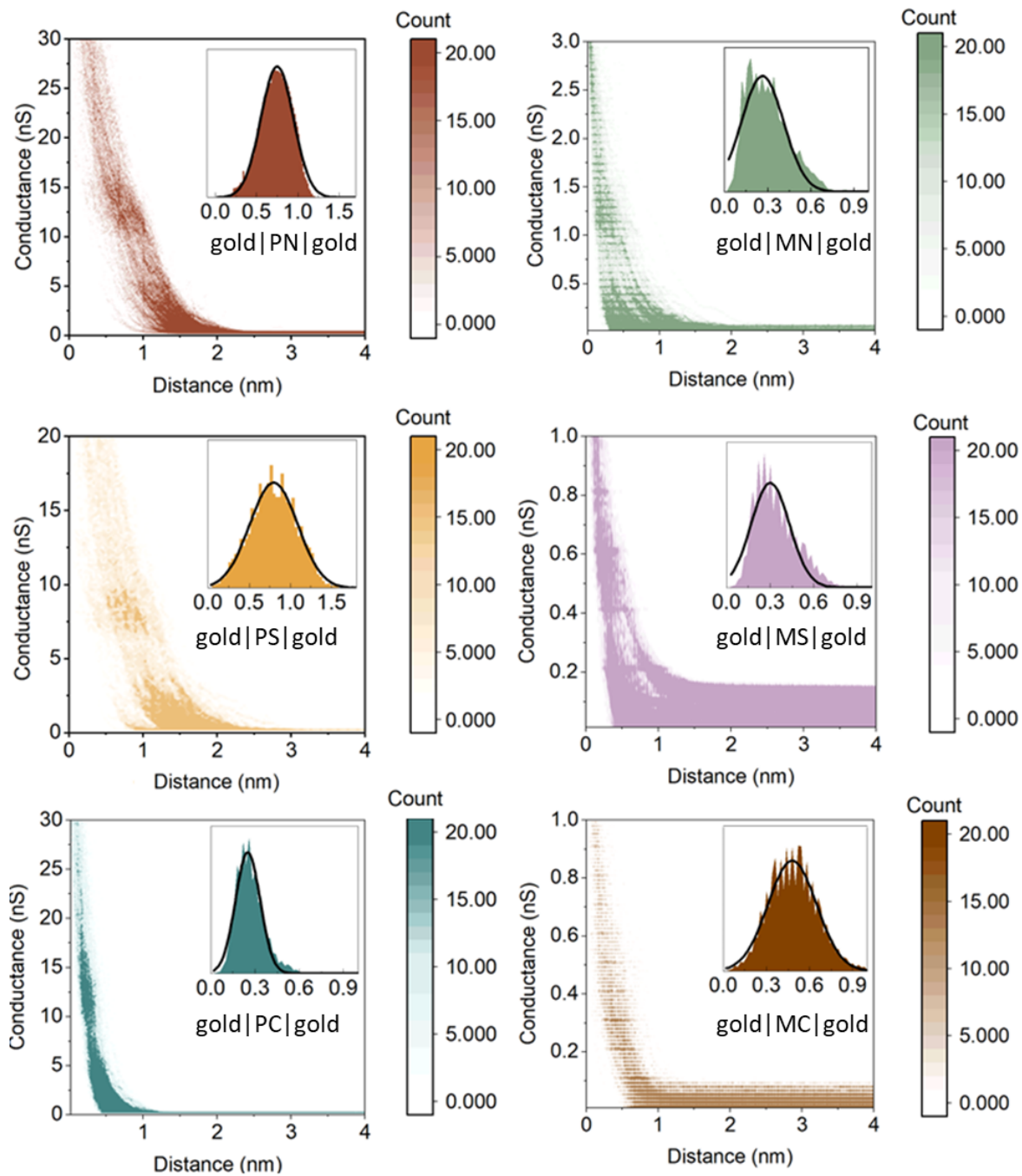


Figure S3 2D conductance-distance histogram of studied gold|molecule|gold molecular junctions. The insets are the Sw of corresponding molecular junctions.

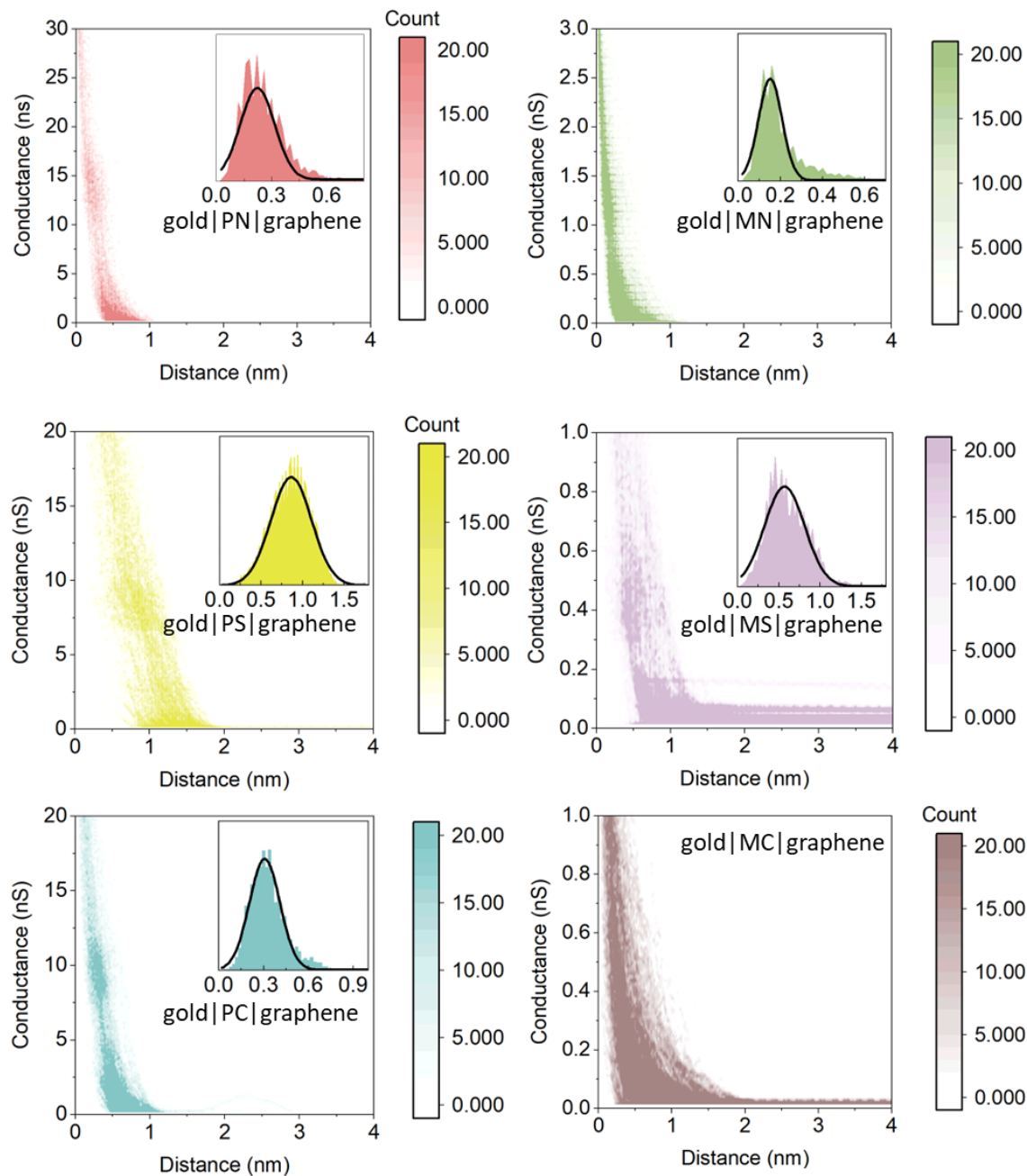


Figure S4 2D conductance-distance histogram of gold|molecule|graphene molecular Junctions. The insets are the Sw of corresponding molecular junctions.

4. Break-off distance

The stretching distance of the entire molecular junction was described by break-off distance ($S_{break-off}$). For STM- $I(s)$ technique, break-off distance consists of initial set point distance (S_0) and plateau length S_w .³⁻⁶ The S_0 is determined by the displacement

distance between the point contact break and tip-substrate separation corresponding to the set point current (I_0). The calculation details of S_0 are described in detail in our previously published article.⁷ The S_w is the end of the current plateau in $I(s)$ curves.⁸ The S_w is obtained by statistically analysing the distance corresponding to the molecular conductance range in the 2D conductance-displacement histogram. Table S1 summarises the S_0 , S_w and $S_{break-off}$ of studied molecular junctions.

Table S1. S_0 , S_w and $S_{break-off}$ of studied molecular junctions

Molecules	S_0	S_w	$S_{break-off}$
Au/PN/Au	0.90	0.74	1.64
Au/MN/Au	0.69	0.34	1.03
Au/PS/Au	0.96	0.78	1.74
Au/MS/Au	1.38	0.31	1.69
Au/PC/Au	1.03	0.25	1.28
Au/MC/Au	1.25	0.48	1.73
Au/PN/graphene	0.80	0.22	1.02
Au/MN/graphene	0.83	0.15	0.98
Au/PS/graphene	0.90	0.85	1.75
Au/MS/graphene	0.72	0.56	1.28
Au/PC/graphene	0.77	0.30	1.07
Au/MC/graphene*	-	-	-

5. Theoretical study of alkyne adsorption on graphene

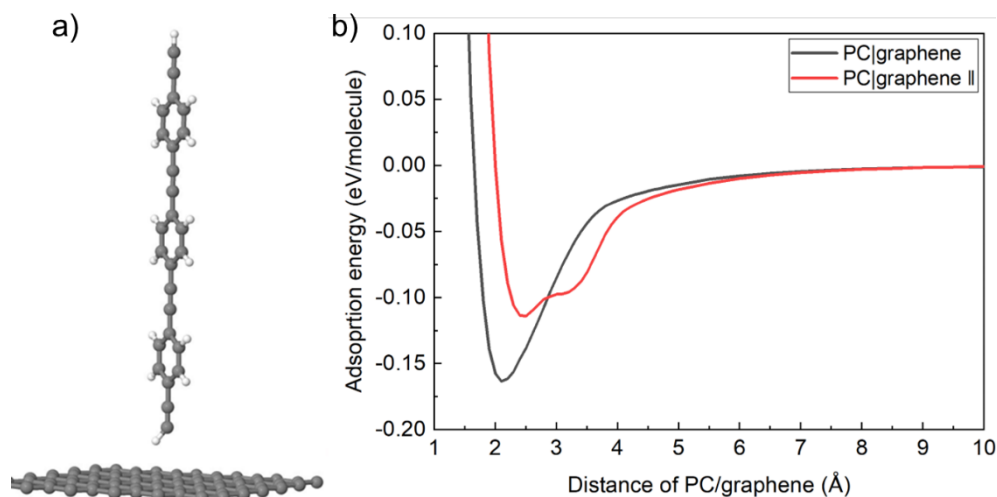


Figure S5 Structural model (a) and adsorption energy vs. distance curves (b) of PC/graphene substrate

Reference

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