

Molecular Platforms as Versatile Building Blocks for Multifunctional Photoswitchable Surfaces

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Supporting Information

Synthesis of the compounds

Synthesis of 4-trimethylsilylethynylpyridine¹ 1.00 g (5.14 mmol) 4-bromopyridine hydrochloride was solved under nitrogen atmosphere in 30 mL triethylamine and 30 mL THF. 300 mg (0.26 mmol) (bis(triphenylphosphine)-palladium(II)-chloride and 40 mg (0.22 mmol) copper(I)iodid were added to this solution. To this suspension were dropped 0.80 mL (5.66 mmol) trimethylsilylacetylene and stirred under reflux for 15 h. The solid was removed and the solvent was evaporated. The crude product was purified by column chromatography (cyclohexane/ethylacetate, 4:1). The product was obtained as light yellow oil (566 mg, 3.17 mmol, 62 %). ¹H-NMR (500.1 MHz, acetone-d₆, 300 K, acetone) δ = 8.58 (d, ³J = 4.3 Hz, 2H), 7.37 (d, ³J = 4.3 Hz, 2H), 0.26 (s, 9H) ppm.

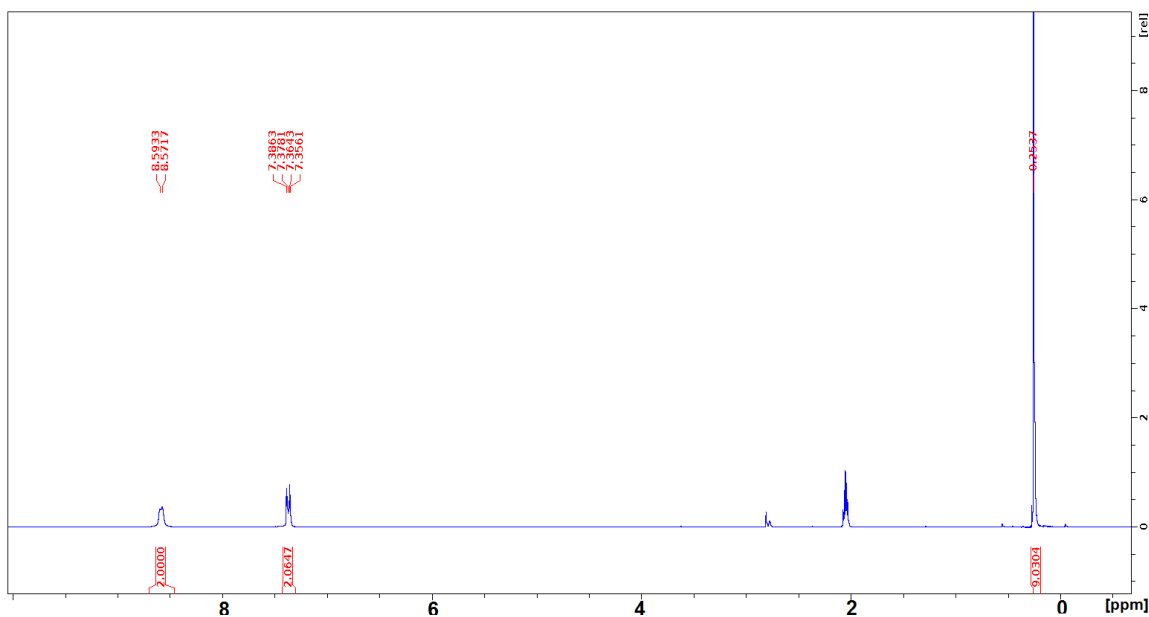


Figure S1: ¹H-NMR spectrum of 4-trimethylsilylethynylpyridine.

Synthesis of 12-(4(pyridine)ethynyl-4,8,12-tri-*n*-octyl-4,8,12-triazatriangulene

Under nitrogen atmosphere 566 mg (3.17 mmol) 4-trimethylsilylethynylpyridine and 2.24 g (3.17 mmol) 4,8,12-tris-*n*-octyl-4,8,12-triazatriangulenium tetrafluorborat were suspended in 50 mL THF. To this suspension were added 1.24 g (22.2 mmol) fine powdered potassium hydroxide. The suspension was heated for 15 h under reflux. Afterwards the solution was poured onto water. For better phase separation brine was added, the phases were separated, extracted with diethyl ether and the organic phases were dried above magnesium sulfate. The solvent was evaporated and the obtained oil was purified by column chromatography (flurosil, diethyl ether) to obtain a red oil. The oil was solved in a minimum of diethylether, overlayed with pentane and stored for 3 d at -18°C . The product precipitates as light pink solid (1.49 g, 2.07 mmol, 65 %). $^1\text{H-NMR}$ (500.1 MHz, acetone- d_6 , 300 K, acetone) $\delta = 8.37$ (d, $^3\text{J} = 4.5$ Hz, 2H), 7.21 (t, $^3\text{J} = 8.3$ Hz, 3H), 6.96 (d, $^3\text{J} = 4.5$ Hz, 2H), 6.67 (d, $^3\text{J} = 8.3$ Hz, 6H), 4.00 (t, $^3\text{J} = 7.6$ Hz, 6H), 1.83 (ps. qui., 6H), 1.49 (ps. quint. 6H), 1.37 (ps. qui., 6H), 1.32-1.21 (m, 18H), 0.86 (t, $^3\text{J} = 6.9$ Hz, 9 H) ppm. $^{13}\text{C-NMR}$ (125.1 MHz, acetone- d_6 , 300 K, acetone) $\delta = 150.49, 141.48, 132.08, 129.60, 126.01, 110.54, 106.19, 99.28, 82.07, 46.68, 32.57, 30.39, 30.23, 30.08, 30.05, 27.46, 26.76, 23.29, 14.35$ ppm. **MS** (ESI): $m/z = 722.5$ $[\text{M}+\text{H}]^+$, 618.6 $[\text{TATA}]^+$

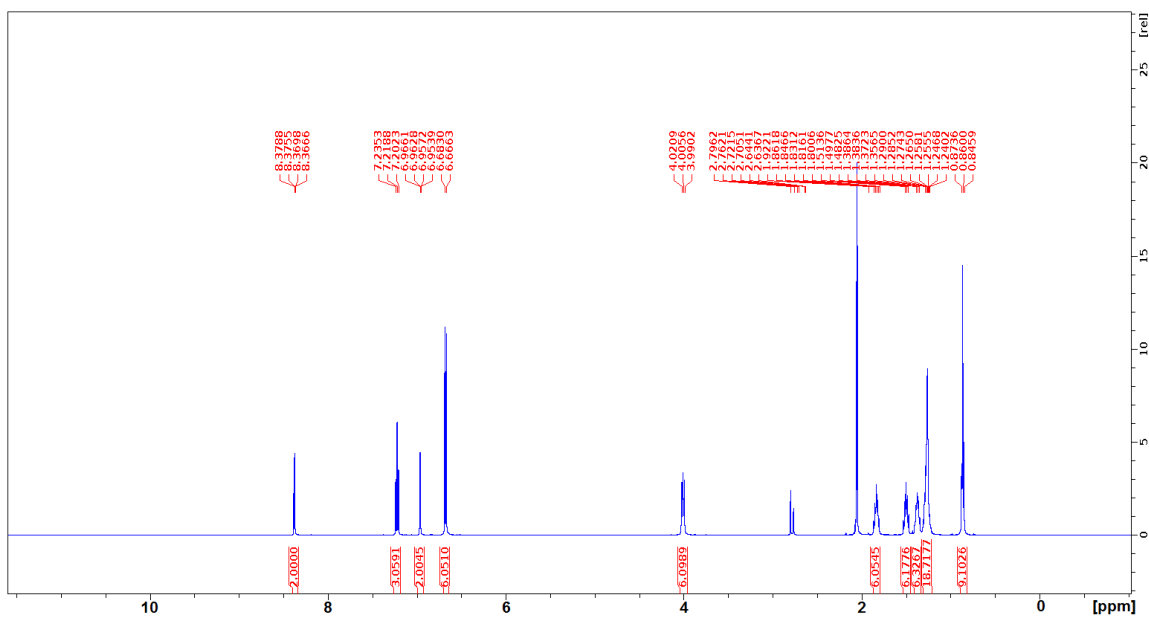


Figure S2: $^1\text{H-NMR}$ spectrum of 12-(4(pyridine)ethynyl)-4,8,12-tri-n-octyl-4,8,12-triazatriangulene.

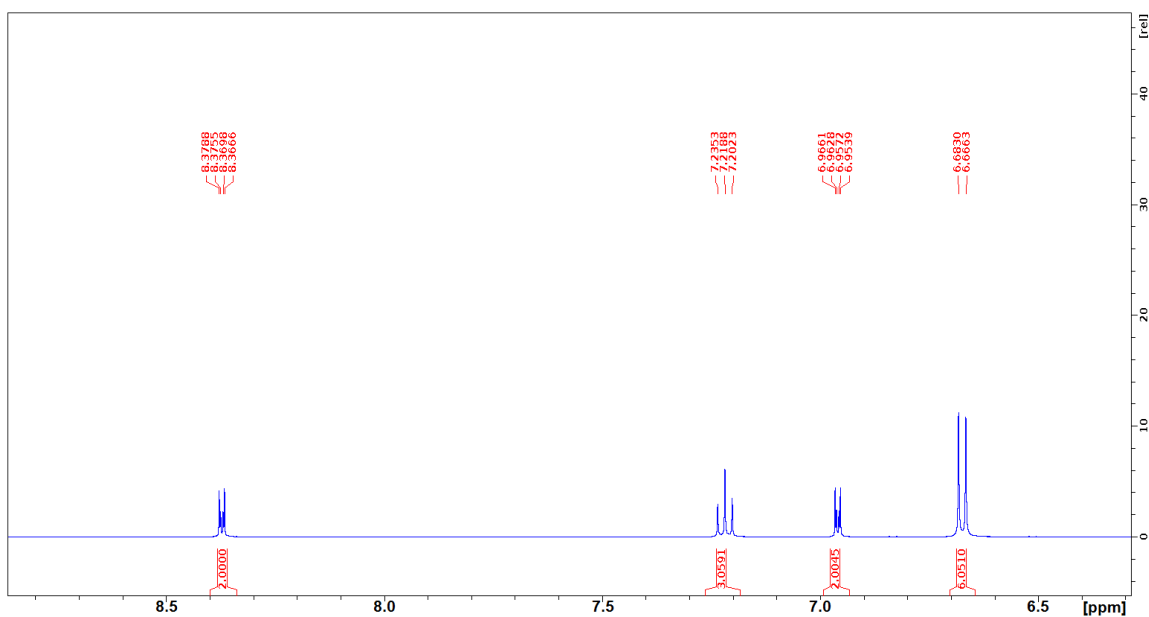


Figure S3: Aromatic region of $^1\text{H-NMR}$ spectrum of 12-(4(pyridine)ethynyl)-4,8,12-tri-n-octyl-4,8,12-triazatriangulene.

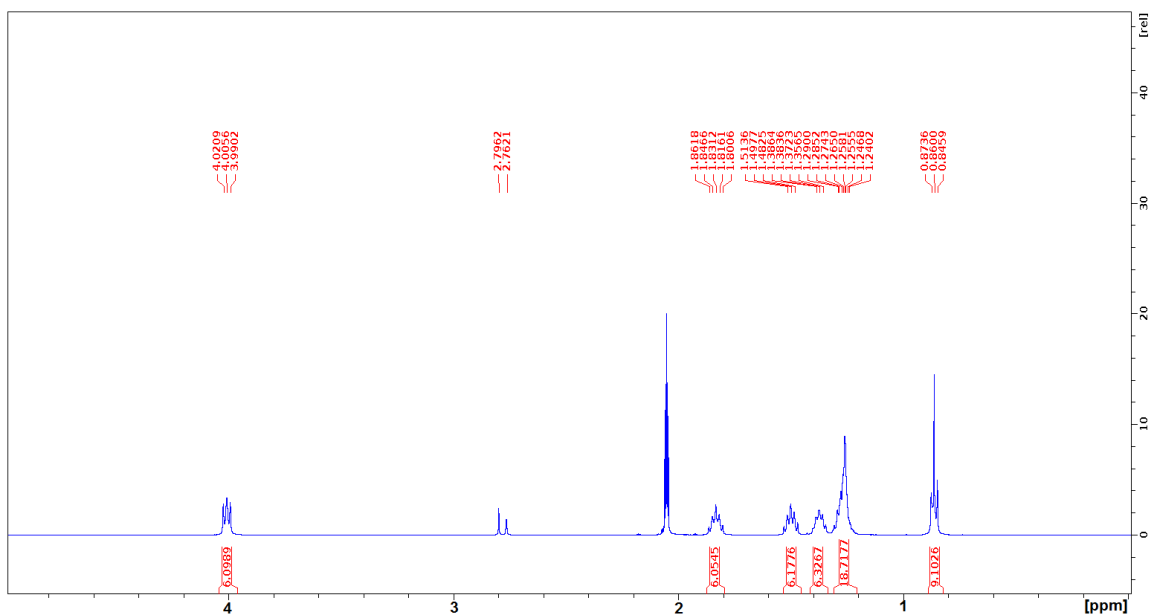


Figure S4: Aliphatic region of ^1H -NMR spectrum of 12-(4(pyridine)ethynyl-4,8,12-tri-n-octyl-4,8,12-triazatriangulene).

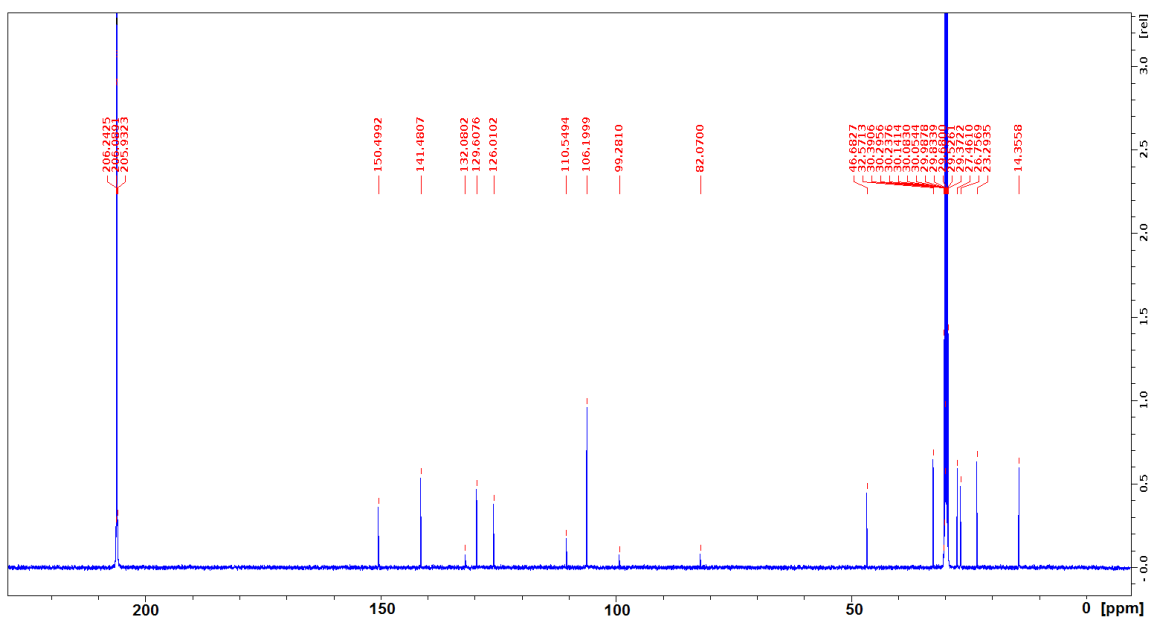


Figure S5: ^{13}C -NMR spectrum of 12-(4(pyridine)ethynyl-4,8,12-tri-n-octyl-4,8,12-triazatriangulene).

Adlayer preparation

Au(111) single crystals with surface diameters of 10 mm, oriented within 0.3° (MaTeck) were used as substrates. The glassware used for the preparation of the SAMs was previously cleaned in piranha solution (1/3 hydrogen peroxide, 2/3 sulfuric acid). Directly before adlayer preparation, the substrates were flame annealed in butane gas. Then, the adsorbate layers were prepared by immersion in toluene solutions (3 ml) containing the respective compounds for 1 hour at temperatures between room temperature and 80°C . These solutions were prepared by mixing 10 μM solutions of the pure compounds at the corresponding ratio. Afterwards, the samples were rinsed with pure toluene to remove excess molecules physisorbed on top of the SAM, dried under ambient conditions, and immediately afterwards mounted in the STM sample holder.

STM measurements

STM studies were performed under ambient conditions with a PicoPlus STM (Agilent, Santa Clara, USA) and mechanically cut Pt/Ir (70:30) tips. The measurements were carried out in constant current mode at tunneling currents of 20 to 50 pA and bias voltages of 200 to 400 mV. The lattice constants and angles between rotational domains were analyzed using SPIP 6.7.6 (Image Metrology). STM images of highly oriented graphite were used for the in-plane calibration. Lateral drift was corrected with a dedicated software, developed by our group.

Quantitative analysis of the STM images

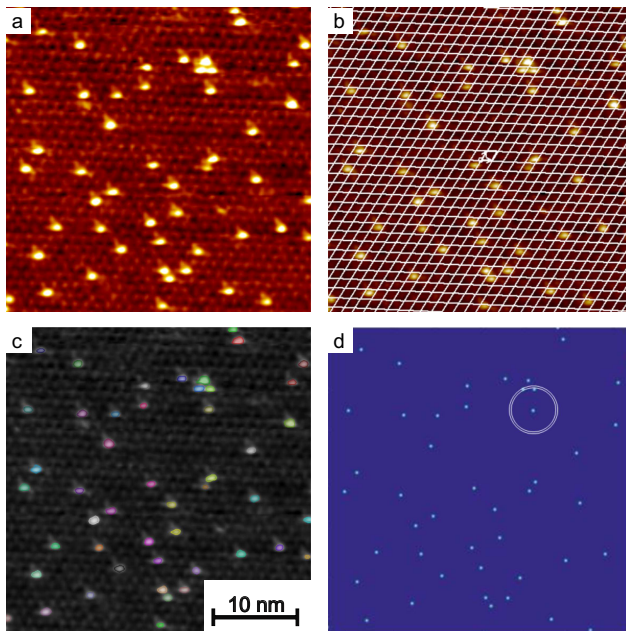


Figure S6: Evaluation steps for the analysis of the STM data of binary mixed adlayers on Au(111): (a) STM image after correction of lateral drift, (b) STM image with an overlaid lattice resulting from the Fourier analysis, (c) detection of molecules obtained with SPIP (the colored circles show the detected molecules), (d) geometric centres of the in (c) detected molecules plotted with Matlab, the circular rings show exemplarily in which area the molecules were counted.

After the STM images had been corrected for lateral drift (Figure S5 a), the superstructure was determined using a Fourier analysis (Figure S5 b). To determine the coverage ratio, one type of molecules was detected and counted by SPIP's particle analysis (Figure S5 c). The total number of adsorption sites could be concluded from the size of the image sections and the previously determined superstructure and thus the coverage could be calculated. The errors for the surface coverage were determined from the maximum deviation.

The Warren Cowley coefficient $\alpha(r)$ can be used as a measure of short-range order for binary mixed adlayers and was calculated as follows:

$$\alpha(r) = 1 - \frac{\rho_{1,i}(r)}{\theta_{1/2}} \quad (1)$$

Therein, $\rho_{1,i}(r)$ is the probability to find a molecule of type **2**, **3** or **4** in a defined distance to a molecule of type **1** and $\theta_{1/2}$ is the coverage ratio $\frac{\theta_1}{\theta_i}$ with $i=2,3,4$.

The Warren Cowley coefficients shown in Figure 3 and S9 show average values, obtained from 5 to 9 images respectively in the size range of 100 to 1600 nm², using Matlab and SPIP. The analysis was achieved by detecting the individual molecules on the STM images and calculating the geometric center. In order to determine the number of molecules of one type in the given distance to the other type, the relevant molecules were counted in the range of circular rings with a radius of the particular distance (1, $\sqrt{3}$, 2, $\sqrt{7}$, 3 nearest neighbour distances) and a width of 0.6 nm (see Figure S5 d). The errors plotted were calculated by error propagation using the standard deviation from the mean. For the calculation of the coverage ratio as well as for the Warren Cowley coefficients, only sections that do not show rotational domains or gold steps were selected, as these would falsify the calculations.

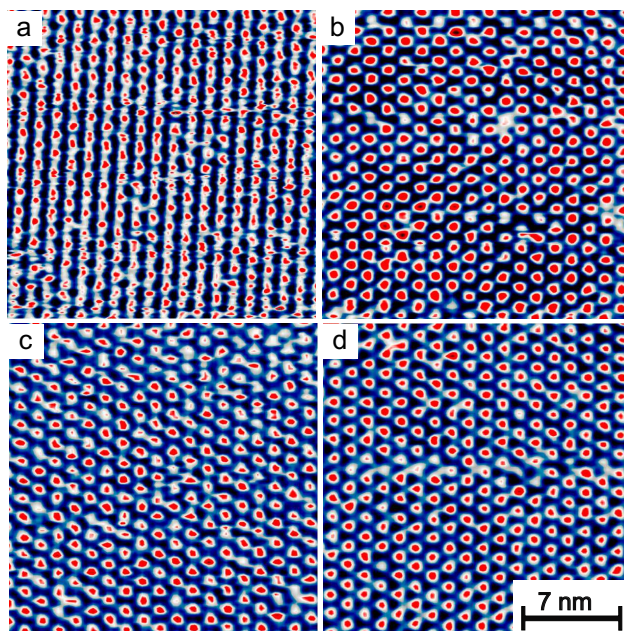


Figure S7: STM images (20 x 20) nm² of self-assembled monolayers of (a) **1**, (b) **2**, (c) **3** and (d) **4** on Au(111).

STM measurements reveal a hexagonally ordered superstructure with intermolecular distances of (1.27 ± 0.04) nm and rotational angles of $12^\circ \pm 2^\circ$ for adlayers of **3**. The lattice constant and the angle between different rotational domains are in agreement with a

$(\sqrt{19} \times \sqrt{19}) R23.4^\circ$ superstructure.

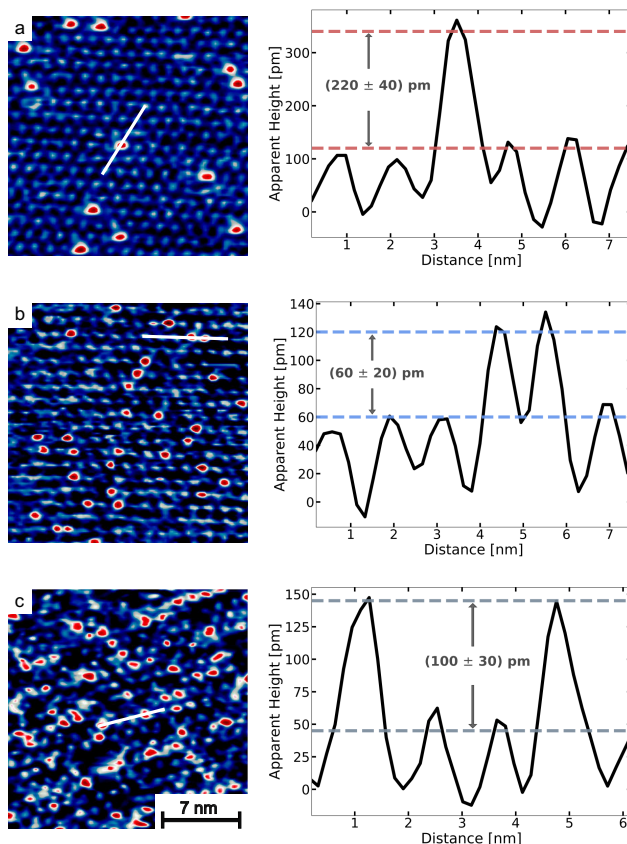


Figure S8: STM images of self-assembled monolayers on Au(111) prepared by coadsorption of (a) 9.8 μM **1** and 0.2 μM **2** solution, (b) 5 μM **1** and 5 μM **3** solution and (c) 5 μM **1** and 5 μM **4** solution (all images sections are 20 × 20 nm² large). The drawn white lines indicate where the crosssections are, which are shown on the right. The dashed lines show average values for the different apparent heights from which the difference in apparent height was determined.

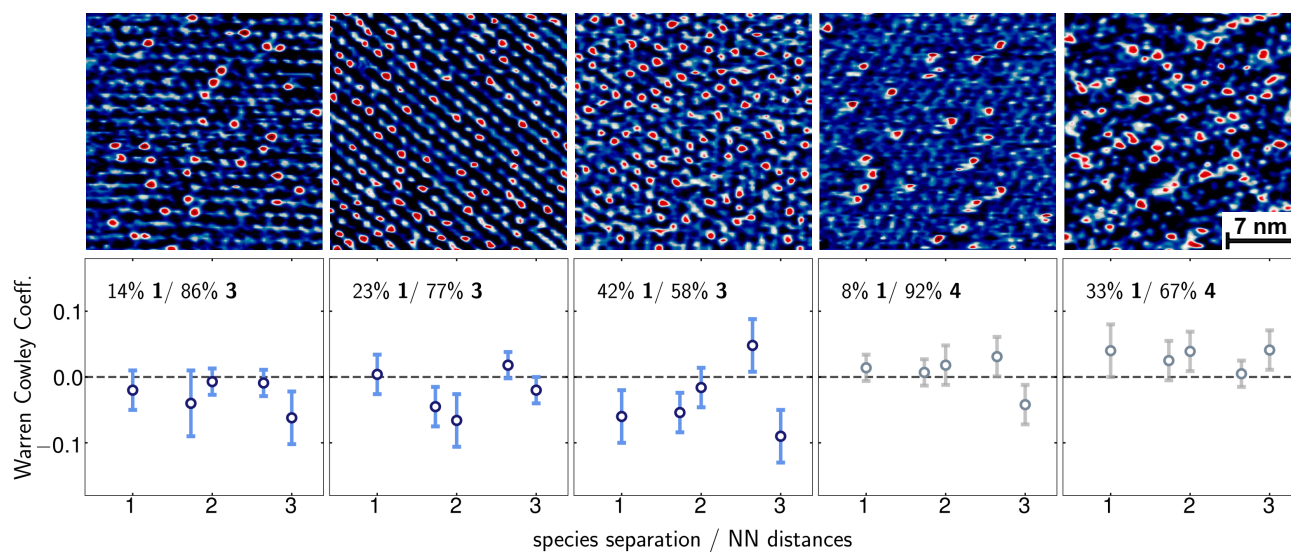


Figure S9: Top: Exemplary STM images of three different compositions of mixed monolayers consisting of **1** and **3** (image 1 to 3 from left to right) and two compositions of mixed monolayers consisting of **1** and **4** (image 4 and 5 from left to right), recorded at $V = 0.3$ V, $I = 20$ pA up to 50 pA, (20×20) nm². Bottom: Warren Cowley coefficients for different surface compositions and distances. The circles represent the coefficients calculated from the STM data and the error bars show the statistical scattering. The dashed line illustrates the value expected for a random distribution.

References

1. Gao, W.-Y.; Yan, W.; Cai, R.; Williams, K.; Salas, A.; Wojtas, L.; Shi, X.; Ma, S. A pillared metal–organic framework incorporated with 1,2,3-triazole moieties exhibiting remarkable enhancement of CO₂ uptake. *Chemical Communications* **2012**, *48*, 8898.