Supporting Information

Molecular Stacking on Graphene

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SI. Experimental section

Materials
The polymethyl methacrylate (PMMA) supported CVD graphene (1×1 cm²) was purchased from ACS Material Co. (USA). Chemicals and solvents including 3-picolylamine, cis-dichlorobis(2,2'-bipyridyl)ruthenium, triphenylphosphine (4-methylbenzenethiol, respectively) and cyclohexanone were purchased from Sigma Aldrich Co. (Germany) and were used without further treatment. The ethanol solvent was treated over preheated molecular sieves (4Å) for three days to eliminate the contained moisture and then introduced into a glovebox (<0.1 ppm O₂, <0.1 ppm H₂O) for use. Si/SiO₂ wafers (300 nm oxide layer) were purchased from Fraunhofer-Institute in Erlangen and cleaned by immersion into isopropanol for a ultrasonic treatment (300 W) for 5 min before use.

Raman spectroscopy
The Raman spectroscopic characterization was carried out on a Horiba Jobin Yvon LabRAM Aramis. A laser (Olympus LMPlanFl50x, NA 0.50) with an excitation wavelength of 532 nm, intensity of 8 mW and a spot size of ~ 1 μm was used. The spectrometer was calibrated by using crystalline graphite. Spectral data was obtained through a motorized x-y table in a continuous line scan mode (SWIFT-module). The temperature-dependent Raman measurements were performed in a Linkam stage THMS 600, equipped with a liquid nitrogen pump MS94 for temperature stabilization under a constant flow of nitrogen. Before measurement, the setup was exhausted with nitrogen for 20 min to completely remove oxygen. The measurements were carried out on Si/SiO₂ wafers with a heating rate of 10 K/min.

Scanning electron microscopy-energy dispersive X-ray spectroscopy (SEM-EDS)
Scanning electron microscopy-energy dispersive X-ray spectroscopy was performed on a FE-SEM (Auriga, Carl Zeiss) equipped with an oxford X-max 80. The working conditions were set at an operating accelerating voltage of 10 kV, working distance of 7.3 mm, the elevation angle of the detector was 35° and the sample was vertically aligned with respect to the secondary electron emission.

Atomic force microscopy (AFM)
Atomic force microscopy was carried out using a Bruker Dimension Icon microscope in tapping mode in air. Bruker Scanasyst-Air silicon tips on nitride levers with a spring constant of 0.4 N m⁻¹ were used to obtain images resolved by 1024 x 1024 pixels. Gwyddin software was used for image processing.

Kelvin probe force microscopy (KPFM)
KPFM images were recorded on a JPK Nanowizard 3 machine with non-contact mode using Cr/Pt
coated tips (AFM Tips: Cr/Pt coated multi 75E-G Budget Sensor Probes, k=3N/M; f = 75kHz). For KPFM a conventional amplitude modulated double pass configuration was used. In the first scan the topography is received and in the second pass the potential profile is measured while keeping the tip at a constant distance of 50 nm from the sample surface.

X-ray Photoelectron Spectroscopy (XPS)

XPS was performed using a monochromated Al Kα source. The measurements were conducted at an emission angle of 0° relative to the surface normal, leading to a spot size of 0.25 mm²; for further details on the setup see ref. S1. The data was evaluated using the software CasaXPS 2.3.18. For quantification, the absolute areas under the respective peaks were set in relation to the C 1s peak area and were adjusted by atomic sensitivity factors (ASFs). The binding energy was calibrated using the literature binding energy value for graphene of 284.9 eV.[S2]

S2. Experimental procedures:

Synthesis of pyridine-3-diazonium tetrafluoroborate

A solution of 1.5 g 3-picolyamine (13.8 mmol) in 10 mL tetrahydrofuran (THF) was cooled down to 0°C using an ice/water bath. Then, 1.3 mL (1.82 g, 20.7 mmol) HBF₄ was added and stirred for 5 min. Afterwards, 2.3 mL (1.99 g, 16.9 mmol) iso-pentylnitrite was dropwise added to the solution, which was stirred for 20 min at 0°C. The white precipitate was filtered off, washed with 50 mL cooled diethylether, and then dried under vacuum – permanently cooling with the aid of an ice/water bath. Here, the synthesized 3-aminoethylpyridine diazonium salt was dissolved in d-ethanol for ¹H-NMR characterization, and the precursor (3-picolyamine) was also characterized for comparison (Figure S1). The details of ¹H-NMR spectra of precursor (3-picolyamine) and target 3-aminoethylpyridine diazonium salt are shown below:

¹H NMR (400 MHz, (CD₃)₂CO, TMS, ppm) δ = 8.58 (s, 1H, Ar), 8.44 (d, J = 4.8 Hz, 1H, Ar), 8.08 (d, J = 7.8 Hz, 1H, Ar), 7.57 (q, J = 12.9 Hz, 1H, Ar), 4.43 (s, 2H, CH₂), 3.71 (s, 2H, NH₂).

¹H NMR (400 MHz, CD3CD2OD, TMS, ppm) δ = 8.73 (s, 1H, Ar), 8.63 (d, J = 4.8 Hz, 1H, Ar), 7.74 (d, J = 8.0 Hz, 1H, Ar), 7.30 (q, J = 12.8 Hz, 1H, Ar), 4.27 (s, 2H, CH₂).

Clearly, after diazotization of 3-picolyamine to form the target 3-aminoethylpyridine diazonium salt, in addition to the slight shift of the entire H signals, the H signal of NH₂ group was disappeared as expected due to the formation of diazo groups (-N₂BF₄). In addition, no other H signals were detected, ruling out the formation of by-product such as diazo ether.
Moreover, FTIR spectrum shows clear N$_2$ and B-F vibrational peaks located at 2284 cm$^{-1}$, and 1052 cm$^{-1}$, respectively, further consolidating the formation of the target 3-aminoethylpyridine diazonium salt. Altogether, it is convinced that the 3-aminoethylpyridine diazonium salt was successfully prepared.

![Figure S1](image)

**Figure S1.** A) $^1$H NMR of precursor 3-picolylamine and target 3-aminoethylpyridine diazonium salt, and B) FTIR spectrum of 3-aminoethylpyridine diazonium salt. Asterisk indicates solvent peaks of (CD$_3$)$_2$CO and CD$_3$CD$_2$OD.

**Pattern preparation by e-beam lithography**

Following a typical wet transfer technique,$^3$ the PMMA-protected graphene monolayer was deposited on a Si/SiO$_2$ wafer. Afterwards, the PMMA coating was removed by a treatment with acetone vapor (60 min) and the wafer was dried in air. Then this surface-deposited graphene monolayer was recovered with a double Polymethylmethacrylate (PMMA) layer (PMMA 200 k 100 nm, PMMA 950 k 200 nm) via spin-coating, followed by a bake treatment for each layer (Layer 1: 180 °C, 60 s; Layer 2: 180 °C, 90 s). Subsequently, the FAU pattern in the double layer was created by using e-beam lithography with a Zeiss Supra SEM (10kV). Such conditions avoid any radiation-related defects in the graphene layer.$^4$ Irradiated PMMA areas were easily rinsed by an isopropanol-methyl isobutyl ketone solution.

**Chemically ligating of multiple molecular bricks**

The first step of a covalent molecular stacking is realized by a reductive functionalization protocol.$^5$ In specific, inside the glovebox (<0.1 ppm O$_2$, <0.1 ppm H$_2$O, Ar), the above prepared patterned graphene
monolayer was reduced by a Na/K (molar ratio 1:3) alloy. To this end, a drop of liquid Na/K alloy was dripped onto the surface of the sample and kept for 1.5 h, leading to the sufficient reductive activation of graphene, which showed a high reactivity towards electrophiles such as diazonium salts. Once the Na/K alloy was blown away by Ar, one drop of the above prepared pyridine-3-diazonium tetrafluoroborate dissolved in dried and degassed ethanol (0.5 mmol/mL) was added and the reaction was quenched after 15 min by the addition of ethanol and the sample was subsequently exported from the glove-box. After additional washing with 20 mL ethanol and 20 mL water, the remaining PMMA layer was dissolved by acetone, giving rise to the 2D-functionalized sample G1. The next step of coordination reaction was performed by directly reacting G1 with cis-dichlorobis(2,2'-bipyridyl)ruthenium (5 mg, 0.01 mmol) in a hot ethanol/water (30 mL, v/v=1:1) solution (temperature below 100 °C) overnight. In this course, the second molecular building unit, namely cis-dichlorobis(2,2'-bipyridyl)ruthenium, were directly anchored to the initially introduced ethylpyridine anchor units rather than the graphene matrix via a ligand-to-metal coordination. As a consequence, the cis-dichlorobis(2,2'-bipyridyl)ruthenium connector brick was introduced and positioned in the patterned regions of graphene along a longitudinal direction (z-axis), leading to the formation of sample G2. Afterwards, the sample was washed three times with acetone/ethanol/water sequence. Utilizing the bipyridyl connecting unit, the third nano-molecular building block - triphenylphosphine / 4-methylbenzenethiol - was grafted, resulting in the formation of G3a and G3b. Specifically, G2 was reacted with triphenylphosphine (0.2 g, 0.76 mmol) in 60 mL ethanol/water (v/v = 1:1) mixture (90 °C) overnight, and 4-methylbenzenethiol sodium salt (0.12 g, 0.76 mmol) in 60 mL cyclohexanone (60 °C) overnight. Finally, the samples were iteratively rinsed with acetone/ethanol/water sequence.

Reference experiments

In order to further prove the covalent nature of the addend binding of the second (cis-dichlorobis(2,2'-bipyridyl)ruthenium) and third molecular building brick (triphenylphosphine / 4-methylbenzenethiol sodium salt), we carried out respective reference experiments, where the involved nano-molecular bricks were directly reacted with pristine graphene (without a preceding installation of anchor units) under identical conditions. After the same work-up procedure, the obtained samples were characterized by Raman spectroscopy as illustrated in Figure S2. Clearly, the corresponding Raman spectra exhibit the typical characteristics of pristine graphene, without the functionality-induced shifts of the G band and 2D band. In addition, the Raman spectra lack the characteristic Raman bands of cis-dichlorobis(2,2'-bipyridyl)ruthenium. All these results indicate that no coordination of the cis-dichlorobis(2,2'-bipyridyl)ruthenium building unit takes place due to the lack of the corresponding
coordination position provided by the initially implemented ethylpyridine anchor bricks, which in turn affect the addition of the subsequent triphenylphosphine / 4-methylbenzenethiol building units. On the other hand, these results strongly support the covalent binding nature of the individual components in the samples G2 and G3a/G3b.

![Figure S2](image1)

**Figure S2.** Raman spectra of the G2 (A(II)), G3a (B(II)) and G3b (C(II)) and the corresponding reference experiment-based products (A(I), B(I), and C(I)).

![Figure S3](image2)

**Figure S3.** Elemental composition of G2 by EDS measurement. The inset shows the presence of Cl in the detected region.

**AFM analysis**

In principle, AFM can facilely probe surface topographic changes of graphene derivatives at a high resolution of several nanometers. However, for our samples, two important external factors affecting surface topography changes of graphene derivatives measured by AFM should be noted. First, due to the typical wet transfer technique, various defects such as wrinkles/folds/cracks/bilayer regions appear on the surface-deposited monolayer graphene (as shown in Figure 4, 5 and 6). These existing defects
exhibit obvious topographic (height) variations and thus affect the corresponding topography (height) changes originating from the introduced functional groups. Second, unfortunately, the fully removal of PMMA from graphene surface remains rather difficult, which represents a classical and typical puzzle in graphene transfer. These PMMA residual domains will also exert a significant impact on surface topography changes of samples caused by patterning functionalization. These two key factors will severely deteriorate the performance (signal-to-noise ratio) of AFM image. Furthermore, the assembled 2D hetero-architectures entails the sequential fusion of three different building blocks, which, however, are not fully rigid and may not remain completely vertical during their stacking, leading to the formation of distinct conformations. As such, less controlled and disordered surface configurations were generated, thereby the obtained AFM image will exhibit significant roughness. Regardless of the roughness, a discernable height variation (~2 nm) was detected from $G_1$ bound with small-sized moieties to $G_3$ equipped with relatively larger grafts, suggesting the molecular stacking in $z$-direction.

**XPS analysis of $G_{3a}/G_{3b}$.**

The XPS spectra of $G_{3a}$ showed charging. Nevertheless, after binding energy correction the data is used for identifying the surface species. The C 1s spectrum shows a dominating peak, which was calibrated to 284.9 eV (Figure S5a). The spectra show only a very weak shoulder at higher binding energy at 286.8 eV, indicative of a minor degree of oxidation [S6]. In the Ru 3d region, two small signals at 282.1 and 281.3 eV were observed (Figure S5b). The binding energy of Ru 3d located at 281.3 eV agrees well with the value of 281.4 eV observed for a ruthenium tris-bipyridine complex [S7]. The Ru 3d located at 282.1 eV can be ascribed to remaining/unreacted Ru-Cl bond within the second building blocks that are not bound to the third building blocks-triphenylphosphine during the last step of reaction. Besides, the N 1s signal at 400.0 (± 0.8) eV (Figure S5c), again fits to the literature position of nitrogen bound to ruthenium (400.6 eV).[S7] These results clearly demonstrate the covalent nature of the attachment of different molecular building blocks, in good accordance with the SEM-EDX and KPFM results. Similar results were observed for $G_{3b}$, where the detected Ru 3d and N 1s bonding energy were located at 281.5 eV and 400.6 eV, respectively. These results are in perfect agreement with reported binding energy of Ru (281.4 eV) and N (400.6 eV) within tris-bipyridine complex [S7], suggesting the covalent nature of $G_{3b}$ as well. Unfortunately, for our radiation source the rather small photoionization cross section of P (0.01621) and S (0.02265) (which are significantly smaller than that of Ru-0.1717) coupled with the charging effect prevent us from reliably identifying their spectra. Based on the XPS spectra, we were able to calculate the amount of the building blocks involved in the constructed architectures localized at the detected spot (not the entire graphene surface). Since charging differed between the individual
measurement regions, the N 1s binding energy position of the C 1s-corrected survey spectrum is used as the most reliable calibration option. For G3a, quantification of the amount of N1s with respect to C 1s gives 3.8 % N per carbon atom, the sum of nitrogen from functional groups introduced in the first and second steps (ethylpyridine and ruthenium polypyridyl complex). Quantification of the amount of Ru 3d relative to C 1s gives 0.14% Ru per carbon atom (0.09 ± 0.03% at 282.1 eV (remaining/unreacted Ru-Cl bond within the second building blocks that are not bound to the third building blocks-triphenylphosphine), and 0.05 ± 0.03 % at 281.3 eV). Thus the first step of reaction can be easily quantified by calculating the amounts of N exclusively belonging to ethylpyridine, which is 3.24% (3.8% - 0.14% * 4) N per carbon atom. The amount of Ru can be directly used to quantify the second step of reaction as 0.14% Ru per carbon atom, and by calculating the Ru and N ratio, the second step of reaction has a yield of ~ 10% - 25%. Following a similar way, for G3b, quantification of the Ru 3d region with respect to the C 1s region yields a degree of functionalization of 0.09 % complexes per carbon atom. The amount of nitrogen was found to be 1.5 %, suggesting a higher yield of the first reaction step of the surface functionalization. Therefore, the first step of reaction can be easily quantified as 1.14% (1.5% -0.09% * 4) N per carbon atom and the second step has a yield of ~ 31%. Notably, the error bar for this quantification is expected to be very large. One has also to be aware that this graphene functionalization is inhomogeneous (a typical and well-known phenomenon in graphene chemistry\cite{S8}), we measured three spots for each sample and they did exhibit significant differences from each other. Given this, here we would refrain from concluding the yields of the entire architectures, and the yields mentioned above only represent the measured spots.

**Figure S4.** Survey of G3a (a) and G3b (b). The binding energy axis is calibrated with respect to the C 1s peak of graphene at 284.9 eV.
Reproducibility of functionalization protocol

To demonstrate the reproducibility of our functionalization protocol, we prepared five samples in parallel for each reaction step. The reactions were monitored by Raman spectroscopy, and the corresponding Raman spectra were shown in Figure S6. The high intense Raman D band as well as the respective upshift/downshift of G-, and 2D-band (compared to pristine graphene) of G_1 for each sample illustrated in Figure S6A indicate the success and excellent reproducibility of first-step reaction (reductive activation reaction). For each G_1, the subsequent binding of cis-dichlorobis(2,2’-bipyridyl)ruthenium via Ru-to-ligand coordination reaction (second step of reaction) yielding G_2 is clearly confirmed by the observation of an obvious upshift of the G band to ~1592 cm\(^{-1}\) along with a downshift of the 2D band to ~2670 cm\(^{-1}\) as cis-dichlorobis(2,2’-bipyridyl)ruthenium represents an electron-donating binding entity (Figure S6B). This was further corroborated by the detection of one of the characteristic Raman signatures of cis-dichlorobis(2,2’-bipyridyl)ruthenium in sample G_2 at 1487 cm\(^{-1}\) (Figure S6B). Moreover, further upshift of the position of the G band to ~1595 cm\(^{-1}\) and downshift of the 2D band to ~2668 cm\(^{-1}\), detected in samples G_{3a} and G_{3b} for each sample (Figure S6C and S6D) corroborate the successful grafting of the third electron-donating building unit via Ru-to-ligand coordination reaction. Based on these results, the excellent reproducibility was experimentally demonstrated as expected.
Figure S6. Raman spectra of the first-step reaction to prepare G₁ (A), second-step reaction to prepare G₂ (B), and third-step reaction to prepare G₃a (C) and G₃b (D). For each step, five samples were prepared and labelled S₁-S₅.

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