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Dynamic covalent conjugated polymer epitaxy on graphene

Lea Assies,^{1,2} § Chaoying Fu,^{3,4,5} § Petr Kovaříček,^{1,*} Zdeněk Bastl,¹ Karolina A. Drogowska,¹ Jan Lang,⁶ Valentino L. P. Guerra,¹ Paolo Samorì,³ Emanuele Orgiu,^{5,*} Dmitrii F. Perepichka,^{4,*} Martin Kalbáč^{1,*}

¹ J. Heyrovsky Institute of Physical Chemistry of the Czech Academy of Sciences, Dolejškova 2155/3, 182 23 Prague, Czech Republic

² Department of Chemistry & IRIS Adlershof, Humboldt-Universität zu Berlin, Brook-Taylor Str. 2, 12 489 Berlin, Germany

³ University of Strasbourg, CNRS, ISIS UMR 7006, 8 allée Gaspard Monge, F-67000 Strasbourg, France

⁴ Department of Chemistry, McGill University, 801 Sherbrooke Street W., Montreal, QC, Canada H3A 0B8

⁵ INRS, Énergie Matériaux Télécommunications Centre, 1650 boulevard Lionel-Boulet, Varennes (Québec) J3X 1S2, Canada

⁶ Department of Low Temperature Physics, Faculty of Mathematics and Physics, Charles University, V Holešovičkách 2, 180 00 Praha 8, Czech Republic

* martin.kalbac@jh-inst.cas.cz *emanuele.orgiu@emt.inrs.ca *dmitrii.perepichka@mcgill.ca
*petr.kovaricek@jh-isnt.cas.cz

§ These authors equally contributed to the work

Abstract

Hybrid heterostructures formed from ordered molecular layers on bidimensional materials can have unique properties differing from those of their bulk phases. By employing principles of dynamic covalent chemistry, we have synthesized a series of novel conjugated polyimines that form epitaxial ordered monolayers on graphene. The interplay between molecular physisorption and dynamic polymerization at the solid-liquid interface drives the formation of longer chains at the surface with higher rates than in solution. The physico-chemical properties of such assemblies at different length scales on graphene were investigated by a combination of experimental techniques. 'Covalent dynamic epitaxy' was also found to modulate the properties of both substrate and dynamers such as doping and photoluminescence, respectively.

1 Introduction

Mastering the mutual interactions at the interface between molecules and two-dimensional (2-D) materials holds great potential to generate novel hybrid 2-D materials displaying a desired set of physical properties.¹⁻⁵ Among 2-D materials, graphene is a well-known platform possessing atomic flatness combined with exceptional opto-electronic characteristics,⁶⁻⁹ high transparency and mechanical robustness.¹⁰⁻¹³ It has been well documented that molecules can form crystalline epitaxial architectures on the basal plane of highly oriented pyrolytic graphite (HOPG).¹⁴⁻¹⁹ In addition, supramolecular epitaxial assemblies can form on individual graphene sheets, and the resulting hybrid heterostructures exhibit atomically precise and periodic patterns that can generate

superlattices.²⁰ It has been shown that employing van der Waals interactions between graphene and supramolecular networks is a powerful strategy to modulate the properties of graphene without perturbing its pristine sp^2 honeycomb lattice,^{21–23} the common drawback of covalent functionalization.^{24–26} On the other hand, weak supramolecular interactions impose different challenges such as lower stability of the lattice, lattice mismatch between graphene and the epitaxial layer, or lattice defects, both in the substrate and the ad layer. All of these factors can be detrimental for the overall properties of the hybrid, and consequently the performance of the final device when such hybrid structures are employed as the active layer.^{27,28}

Here we use principles of dynamic covalent chemistry²⁹ (DCC) to achieve on-surface synthesis of dynamic conjugated polymers – dynamers.^{30–34} When occurring at a solid-liquid interface, dynamic covalent chemistry comprises reversible interactions at both covalent and non-covalent levels. Non-covalent interactions exist between the molecular adlayer and substrate surface.^{20,35} Covalent tethering occurs between *ad hoc* functionalized molecular building blocks which interact through reversible covalent bonds, thereby improving the robustness of the assembly.^{36–38} The reversible nature of the bond formation allowed by DCC enables thermodynamic control and results in highly ordered self-assembled structures.^{16,20,29,35,39} These features make dynamic bonds ideally suited for fabrication of surface-confined architectures including polymers and covalent organic frameworks.^{22,35,40–47} The concept of thermodynamically controlled supramolecular dynamer epitaxy is particularly attractive in the context of conjugated polymers, largely employed as (opto)electronic materials.^{48–51} In our work, we employed novel bifunctional aromatic aldehydes decorated with long alkyl chains to induce self-assembly on sp^2 -carbon surfaces (monolayer graphene and HOPG), and copolymerized them with diamines forming polyimines. The monomers were designed to provide a different degree of conformational flexibility and π -conjugation. In particular, we investigated (i) how the structural information encoded in the molecule's constitution influences the final 2–D dynamic covalent assembly; (ii) how the spectroscopic properties of the final polymer are affected by epitaxial adsorption on graphene and how this adsorption affects the properties of the graphene substrate. The combined results, gathered with a broad arsenal of spectroscopic and microscopy techniques, provide new insights into the dynamic molecule/graphene interface.

2 Results

2.1 Molecular design and synthesis

To explore the dynamic covalent polymerization on graphene, we focused on the prototypical case of imine chemistry, by exploiting aldehyde and diamine building blocks. Three aromatic dialdehydes were synthesized from hydroquinone (**HQ**), resorcinol (**RC**) and 2,2'-biphenol (**BP**) precursors via *O*-alkylation with *n*-octadecylbromide followed by bromination with NBS, lithiation with *n*-BuLi and formylation by *N,N*-dimethylformamide (see SI Section 1). We anticipated that the position at which the aliphatic chains are tethered to the aromatic core would result in different confinement criteria for the polymer self-assembly and, thus, that the information contained in the constitution of each of these monomers would translate into the polymer self-assembly in 2–D space. We chose the following three diamine counterparts: hydrazine (**hd**, which supposedly forms the tightest packed 2–D layers), *p*-phenylenediamine (**pp**, which provides π -conjugation and rigidity but expands the lattice packing), and ethylenediamine (**eda**, which acts as a flexible non-conjugating linker). The overview of the employed structures and their acronyms is provided in Figure 1.

Figure 1 Structures and their acronyms used in the study. Dialdehyde derivatives (**HQ**, **RC**, **BP**) react on both carbonyl groups with diamines (**eda**, **pp**, **hd**) to give a total of nine corresponding polyimines. The polymer identifier is composed of the acronyms of its components, for example of **HQ:hd**.

2.2 Dynamic polymerization process in solution

The polymerization reactions were probed at high concentration (20 mM) by NMR spectroscopy and at low concentration (10 μM) by UV-Vis spectroscopy. While in NMR experiments the reaction occurs without catalytic assistance over several days, the reaction kinetics as monitored by UV-Vis spectroscopy is too slow to be followed experimentally. As reported earlier, the reaction can be catalyzed by acids or amines,^{37,52} which was also confirmed in our experiments by addition of octanoic acid or *n*-propylamine in UV-Vis and NMR experiments, respectively (see SI). The polymers were also synthesized in bulk by mixing the two constituents in a 1:1 ratio and reacting at 60 °C for three days.

The degree of polymerization of **HQ:hd** was determined by gel permeation chromatography (GPC) and diffusion measurement by NMR spectroscopy. The GPC chromatogram shows a relatively broad peak with several maxima corresponding to fractionation and re-equilibration of the dynamer on the column. Molecular weight distribution analysis (see SI Section 8) revealed a dominant mass at around 5 kDa, corresponding approximately to a 7-mer and the smaller peaks correspond to lower oligomers down to the monomer. This result was corroborated using ^1H pulsed field gradient NMR spectroscopy, which estimated a chain size of $n = 8 \pm 2$ (details in SI Section 7). This estimation is in a good agreement with the values obtained from GPC.

The thermodynamic stability of the C=N bond differs for different imine derivatives. Under the conditions employed, the aromatic amines are less stable and prone to exchange by aliphatic amines, which can again be exchanged by hydrazine derivatives.³⁷ However, in the present case, the conjugation extension favours **pp** incorporation into the polymer formed from **eda** giving approximately statistical product ratio. Yet, upon addition of **hd** both diamines are expelled from the

backbone providing exclusively polyazines, as evidenced by characteristic NMR signal shifts (see Figure 2a).

Figure 2 a) Azomethine proton region of the NMR spectra of **HQ** condensed with different diamines and their mixtures. The polymers with **eda** shows two signals at around 8.5 and 8.7 ppm, with **pp** at around 8.9-9.0 and that derived from **hd** at 9.0-9.1. When **eda** and **pp** are put in competition, formation of both products is observed, while addition of **hd** gives exclusively polyazine chains. All spectra are recorded in equilibrium and presence of several signals in each spectrum is due to the dynamic network of polymers in the mixtures. b) Selection of UV-Vis and PL spectra of the starting dialdehyde monomers and the corresponding polymers formed with conjugating diamines linkers **pp** and **hd**. The absorption and emission is redshifted due to conjugation extension upon imine formation. Spectra of other polymer can be found in the SI.

UV-Vis spectra of polymers formed in solution from **pp** or **hd** show an absorption shift towards lower energies indicating extension of the conjugation length by polyimine formation (see Figure 2b and individual traces in the SI). This is further evidenced by photoluminescence (PL) spectra in which the polymerization leads to a red-shifted emission maxima and significant broadening of the band supporting conjugation extension, which is indicative of a dynamic network of polymer chains with various length (Figure 2b). It is important to point out that PL measurements carried out in solution only reflect the effective conjugation length which is shorter than the actual polymer backbone due to conformational disorder. Thus, the emission is red-shifted when the polymer is planarized on the surface. For instance, the emission maximum for the **HQ** monomer occurs at 473 nm, for **HQ:hd** in solution at 475 nm and in a drop-casted film at 550 nm (SI Figure S4), but when measured as a 10 nm film on graphene the emission shifts to 624 nm (Figure 3), *i.e.* by 0.62 eV with respect to the solution.

Figure 3 Photoluminescence spectrum of **HQ:hd** measured with confocal Raman spectrometer (excitation wavelength 532 nm) on a 10 nm thin film on graphene. Strong red shift of the emission is observed to about 624 nm due to planarization of the polymer backbone on the surface.

2.3 Raman spectroscopy of hybrid heterostructures

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Raman spectroscopy is a non-invasive method to investigate solid materials. It is extensively used to determine strain and doping levels in graphene and related 2-D materials,⁵³ and was applied for our epitaxial layers to study the formation of the polymers and their interactions with graphene. Graphene was grown by the chemical vapour deposition method (CVD) on a copper foil, and 1 cm x 1 cm sheets were transferred onto Si/SiO₂ substrates by the Cu etching/polymer assisted method as described earlier (see SI Section 2).^{54,55} The Raman spectrum of the so-prepared samples exhibited only G and 2D modes at around 1600 and 2700 cm⁻¹, respectively, without any detectable D mode (Figure 4a). The PL observed in solution and in thick films is efficiently quenched when the films were deposited on graphene from low-concentration solutions,⁵⁶ and the Raman spectra clearly show the bands corresponding to both the polymers and graphene (Figure 4a). The strain-doping analysis, calculated from the 2D and G band positions,⁵³ was performed on a pristine graphene and after deposition of the dynamer. From the analysis, we find that, while the strain is negligible, the presence of the **HQ:hd** polymer leads to a decrease in graphene's pristine doping from 1.35×10^{13} to 9.66×10^{12} cm⁻², *i.e.* by about 30 % (see SI Section 4.4).

HQ:hd bands are found at 1293 cm⁻¹, 1525 cm⁻¹, and 1573 cm⁻¹ corresponding to the $-(CH_2)_n-$ twisting vibration, the symmetric C=N-N=C stretch of aryl azines, and the C=C stretching vibration of the benzene rings, respectively.⁵⁷ The Raman shift and shape of the CH₂ twisting band are useful probes into the self-assembly of the aliphatic chains^{58,59} – a sharp band closer to 1293 cm⁻¹ indicates high crystallinity while a shift above 1300 cm⁻¹ and band broadening is typical for the amorphous phase. The polymer Raman scattering is most efficient in the excitation range of 458 – 648 nm, presumably due to resonance enhancement. The experimental traces for other polymers with corresponding discussion is provided in the SI Figure S5-6. Raman mapping was used to study if the polymer assembles selectively on graphene *vs.* the bare substrate. The obtained spectra were fitted and (co)localization of the polymer and graphene bands together with optical image was investigated (SI Table 3). A selective film formation on graphene was observed for the **HQ-** and **RC-**based polymers upon varying the concentration of the spin-coated solution, but the **BP** polymers showed poor selectivity, even in highly diluted ($\leq$ nM) solutions of monomers. Excess of spin-coated material can be rinsed with chloroform, but rinsing with solvent does not lead to complete film removal in any case.

Figure 4 a) Raman spectrum of the **HQ:hd** polymer film on glass and spin-coated on graphene on a Si/SiO₂ support. The characteristic polymer bands are clearly visible as well as the graphene G and 2D modes at 1600 cm⁻¹ and 2693 cm⁻¹, respectively. b) Optical image of patterned graphene stripes with an on-surface grown polymer layer (scale bar equals 4 μm). Maps of the intensity of graphene's 2D mode (c) and the polymer band at 1293 cm⁻¹ (d) are fully colocalized and match

the optical image (scale bars equal 4 μm). e) AFM image acquired over the graphene stripe with height profile (f) indicating an average graphene-polymer (on-surface grown at 1 μM monomer concentration) hybrid layer thickness of about 2 nm. Article Online
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To study the on-surface growth of **HQ:hd** on graphene, we have immersed graphene sheets on Si/SiO₂ substrates into **HQ** solution of concentration from 1 mM down to 1 pM. After a 30 minute equilibration period, one equivalent of **hd** was added and the reaction was kept at room temperature for 12 hours. Successful polymer film formation was observed at all concentrations as confirmed by Raman mapping showing co-localization of the graphene 2D mode and a polymer band at 1293 cm⁻¹ (Figure 4b-d and SI section 9.2). Using atomic force microscopy, the layer thickness (at graphene edges or defects) was measured as 10 nm at 1 mM concentration down to about 2 nm at 1 pM level, *i.e.* close to monolayer coverage (see SI for experimental traces). By measuring the height profile over **HQ:hd** self-assembled layers from a 1 μM solution on 3- μm wide graphene stripes, an average hybrid composite thickness of about 2 nm was determined (see Figure 4 e-f). Spin-coating of polymer solutions (0.3 mg/mL) in chloroform provided homogenous ~5 nm thick layers. Raman spectra of all **HQ:hd** films showed a sharp band at 1293 cm⁻¹, thus confirming high crystallinity even in thicker films, in contrast to other polymers which are more disordered (SI Figure S6b).

The surface has a 'catalytic' effect, dramatically accelerating polymerization.^{60,61} Extrapolating from the second-order kinetics measured at a concentration of 20 mM (SI Figure S22), the reaction in 1 nM solution would require more than 10⁷ days to reach equilibrium. However, dynamic self-assembly on graphene is successfully achieved in less than 12 hours. At 1 nM concentration, the polymer layer self-assembly appears continuous by Raman mapping, even though most of the molecules present in the solution must assemble on the surface to form a continuous layer (approx. 1 cm², 25 mL of 1 nM solution). At 1 pM concentration, the polymer Raman bands are not homogeneously mapped over the whole graphene area.

2.4 Surface-templated polymerization

Scanning Tunnelling Microscopy (STM) is a powerful characterization technique capable of imaging surface adsorbed molecules with sub-molecular resolution.^{62–64} We used STM to study the self-assembly and on-surface polymerization yielding macromolecules with controlled shape dictated by the constitution of the starting building blocks. The long octadecyl side-chains in **HQ**-monomers provide not only good solubility in organic solvents, but also a strong physisorption enthalpy on the *sp*² carbon surface. The adsorption energy of a benzene ring on graphite surface is 0.5 ± 0.08 eV,⁶⁵ which is only one fifth of the adsorption energy of two fully extended octadecyl side-chains on graphite surface (~2 × 1.16 eV, ~64.2 meV per CH₂).⁶⁶ The molecular assembly is further stabilized via interdigitation of neighbouring chain lamellar structures. The use of Schiff-base polymerization enables dynamic exchange of the imine constituents at the solid-liquid interface.²⁹

When applying a 1:1 molar ratio mixture of **HQ** and **hd** solution (0.1 mM each) in trichlorobenzene (TCB) and octanoic acid (0.1 % v/v as an acid catalyst) onto an HOPG substrate, the immediate formation of lamellar structures is observed (Figure 5a). Because of the small size of **HQ** and **hd** monomers, the molecular dynamics at this concentration at room temperature is faster than the STM imaging, and thus, they could not be visualized (Figure S16 and S17). Therefore, the appearance of lamellar architectures indicate the *in situ* formation of **HQ:hd** polymers on HOPG, which was also confirmed by UV-Vis measurement of the same solution mixture and by XPS spectroscopy of the film (Figure S13-S15). The area of the long-range ordered single domains often exceeds 100 × 100 nm² and the lamellae are up to ~150 nm long. However atomic resolution could not be achieved to confirm the presence of single or multiple polymer backbones assembled within each lamella.

Figure 5 a) STM image of *in-situ* polymerization of **HQ** and **hd** at the TCB/HOPG interface showing single domain lamellar structures extending 100 nm in two dimensions. b) Self-assembly of bulk-synthesized **HQ:hd** polymers at the TCB/HOPG interface. c) High resolution STM image of **HQ** self-assembly in 1 mM solution at TCB/HOPG interface. The STM image is calibrated with the underlying HOPG lattice, showing a unit cell dimension of $a = 1.0 \pm 0.1$ nm, $b = 3.0 \pm 0.1$ nm and $\alpha = 81 \pm 1^\circ$. d) High resolution STM image of *in-situ* grown **HQ:hd** polymer in 0.1 mM monomer concentration solution at TCB/HOPG interface. The STM image is calibrated with the underlying HOPG lattice, showing a unit cell dimension of $a = 0.9 \pm 0.1$ nm, $b = 2.9 \pm 0.1$ nm and $\alpha = 82 \pm 1^\circ$. e) Molecular modelling shows a topographic similarity between **HQ** and **HQ:hd** polymer lamellae facilitating the on-surface reaction by monomer pre-assembly. The polymer backbone of **HQ:hd** was optimized by DFT calculation at B3LYP/6-31G(d) under periodic boundary conditions.

In comparison with *in situ* surface-grown polymers, we also imaged *ex situ* (i.e. in the flask) synthesized **HQ:hd** polymer drop-casted (0.07 mg/mL in TCB) onto HOPG. In contrast to the extended domains formed during *in-situ* polymer growth, the solution-synthesized polymer aggregates into much smaller domains on HOPG, with an average area of 30×30 nm² (Figure 5b) and 120° mutual orientations respecting the three-fold symmetry of the underlying HOPG (confirmed by 2D-FFT in Figure 5b onset).

High-resolution STM images and molecular modelling indicate very similar unit cell dimensions of the **HQ:hd** polymer ($a = 0.9 \pm 0.1$ nm, $b = 2.9 \pm 0.1$ nm, $\alpha = 82 \pm 1^\circ$) and **HQ** monomer ($a = 1.0 \pm 0.1$ nm, $b = 3.0 \pm 0.1$ nm, $\alpha = 81 \pm 1^\circ$) in the lamellar structures (Figure 5c-e). The molecular modelling also reveals that both the length and angle of the formed C=N-N=C linkage are close to those of the C=O...H-C(=O) hydrogen-bonded assembly of **HQ** (Figure 5e). These topographic similarities suggest that only limited molecular movements in the self-assembled **HQ** structure would be required for the formation of **HQ:hd** polymers, and thus the dynamic pre-assembly of **HQ** on HOPG might facilitate the long-range ordering of the *in-situ* grown **HQ:hd** polymers. This approach is reminiscent of topochemical polymerization of diacetylene derivatives on HOPG, in which the supramolecular ordering of diacetylene monomers favours polymerization within self-assembled monolayers.^{67–70} In contrast, due to the lack of a topographic match between the monomer and polymer assemblies, lamellar structures observed for the *in situ* growth of other polymers based on **HQ**, **RC**, **hd** and **pp**

monomers are much smaller than those of **HQ:hd** polymers (SI, Figure S18). In addition, **BP**-based polymers form no ordered assemblies at all. STM observations of the **HQ:hd** polymer grown on the CVD graphene showed that the lamellar structure formed is identical to that formed on HOPG (SI, Figure S20). However, the image quality is hampered by nano-rugae formed during graphene transfer.^{55,71}

3 Discussion

The thermodynamically driven supramolecular dynamer epitaxy on graphene was investigated for a series of bifunctional aldehydes (**HQ**, **RC**, **BP**) and amines (**hd**, **pp**, **eda**), each combination providing a different dynamer. The polycondensation in solution was monitored by NMR and reached equilibrium in about 6 days. The dynamic nature of the imine bond even when embedded in the backbone was confirmed by complete exchange of **eda** or **pp** from the polymer on addition of **hd**. The polymerization provides a *dynamic network*^{72–74} of **HQ:hd** polymers with average size of about 7–8 units, as determined by DOSY and GPC. In cases of **hd** and **pp** linkers, the polycondensation extends the conjugation and it can be evidenced spectroscopically by absorbance and PL maxima are red-shifted with respect to the monomer.^{75,76}

If the reaction occurs directly on a templating surface such as graphene or HOPG, the length of the polymer chains formed increases by more than an order of magnitude, as observed by STM and corroborated with PL measurements. PL is also very sensitive to molecular conformation rigidity. Thus, self-assembled films on graphene display a large PL red-shift (0.62 eV) as compared to the polymer in solution. In addition to the thermodynamic effect, a dramatic kinetic enhancement of polycondensation was also observed on surfaces compared with in solution. We propose that in the dynamic polymerization process, the graphene surface acts as a template for monomer pre-assembly and thus facilitates the highly ordered surface-confined polymerization. The templating effect could also operate via establishing a high effective concentration of the reactive species at the surface. Furthermore, thanks to the fast imine dynamics and entropically preferred adsorption of larger species on the surface,²⁹ the on-surface polymerization could compete with the adsorption of small agglomerates as in the case of in-solution synthesized polymers, thus rendering fully extended polymer networks.

On a molecular level, the polymers self-assemble into extended (>100 nm) lamellar structures by aliphatic chain interdigitation, as evidenced by STM. This clearly shows that the substrate plays an important role in facilitating the high degree of polymerization of **HQ:hd**. Other dialdehydes do not form large crystalline domains on the surface, confirming that the constitutional design of molecules dictates the final self-assembly. The high crystalline order at a micron scale and larger can be conveniently followed by Raman mapping of the position and shape of the 1293 cm⁻¹ CH₂ twisting band. In agreement with STM results, the behaviour of this twisting band shows that **HQ:hd** films have higher crystallinity than films of other polymers. Raman mapping can also be used to determine the spatial distribution of the deposited polymer (either on-surface grown or spin-coated) on graphene layers by colocalization of the characteristic polymer bands and graphene Raman modes. The preference for graphene substrate decreases with lower film crystallinity: **HQ:hd** has the highest selectivity, **RC**- and **pp**-based polymers show intermediate selectivity, and randomly packed **BP**-based dynamers display essentially no selectivity. This result suggests that feasible epitaxy of the dynamer layer on graphene has a large contribution to the selectivity of this layer. The polymer layer thickness, derived from AFM, can be varied between 2 to 10 nm by adjusting the monomer concentration during the on-surface polymerization.

Spectral separation of the dynamer and graphene Raman signals also allows for the investigation of both layers of the heterostructure simultaneously. Supported graphene is inherently doped by the substrate, which in our case is SiO₂, leading to a rather high doping level ($>10^{13}$ cm⁻², p-doping). After deposition of the dynamer on graphene, we observed a 30 % decrease (approximately) in the doping level, and we propose that this is due to the compensation of the inherent doping by n-doping caused by the polymer layer.

4 Conclusions

In conclusion, the prepared hybrid molecular assemblies are confined to the 1 x 1 cm² graphene substrate with superb resolution and show highly ordered periodic arrangement at the nanoscale. The self-assembly process forms monocrystalline domains extending by areas exceeding 100 x 100 nm². This stems from the interplay of two dynamic processes – adsorption/desorption of monomers on the surface and dynamic covalent polymerization forming polyimine chains. We have shown that the graphene and HOPG surfaces affects the dynamer formation and assembly, both kinetically and thermodynamically, and lead to periodic superstructures, with spectroscopic properties differing from the those observed in solutions containing these conjugated polymers. On the other hand, the assembly is also affecting its substrate by adjusting the doping level. Our results show that supramolecular conjugated dynamer epitaxy on carbon surfaces is an efficient strategy for bottom-up fabrication of hybrid 2–D materials with tunable properties. This concept can be exploited in broad range of (opto)electronic devices such as semiconducting layers, sensors and (light-emitting) diodes. Mastering the underlying covalent dynamics at molecular level can generate hybrid molecule/2D interfaces that feature defect-healing and adaptation to a stimulus. As such, these hybrid interfaces could be exploited as their active layers in devices.

5 Supporting information

Electronic supplementary information (ESI) available: Synthetic protocols, additional spectra and images, polymer preparation and characterization, graphene synthesis and processing.

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