SUPPLEMENTARY INFORMATION

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

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

[§] These authors equally contributed to the work

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1 Synthetic protocols

1.1 General

Starting materials and reagents were purchased from Sigma-Aldrich and used as received. Solvents we purchased from Penta Chemicals and were in *p.a.* quality grade.

¹H- and ¹³C-NMR-spectra were recorded with Varian Mercury 300 Plus 300 MHz NMR with 2-channel broadband Mercury Plus console, Varian 300 H/F/X PFG tunable probe and VNMRJ workstation. Chemical shifts are referenced on the residual solvent signal according to the literature.¹ Multiplicities are described as s (singlet), d (doublet), dd (doublet of doublet), t (triplet), and m (multiplet). Correlation of signals was confirmed by APT, COSY, HMBC, HSQC, and NOESY experiments.

Melting points were determined with the Stuart melting point apparatus SMP20 in open capillaries.

Column chromatography was carried out with silica gel 60 (40 - 63 μ m) and commercially available solvents. Thin Layer Chromatography (TLC) was carried out with pre-coated TLC-sheets ALUGRAM[®] Xtra SIL G/UV₂₅₄ (aluminium coated with 0.2 mm silica gel 60 with fluorescent indicator UV₂₅₄) and visualized by a UV-lamp (365 and 254 nm).

All formylation reactions were carried out in an inert gas atmosphere of argon and under exclusion of air and humidity by using the Schlenk technique, for which the glassware was dried in the oven. All used chemicals and solvents were bought from Sigma-Aldrich and used as delivered. General reaction scheme for the synthesis of dialdehyde monomers is shown in Figure S 1. Yield in protocols is indicated as ω . Dialdehydes based on 4,4'-dihydroxybiphenyl and 1,5-dihydroxynaphthalene were also considered but found synthetically unfeasible.



Figure S 1 General procedure for dialdehyde monomer synthesis. Dihydroxyarenes were first O-alkylated and then brominated. Aldehyde functions were introduced by halogen-metal exchange and subsequent reaction with N,N-dimethylformamide (DMF).

1.2 Synthesis of HQ monomer





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To a solution of hydroquinone (1.67 g, 15.2 mmol) in 65 mL of argon-purged DMF, 1-bromooctadecane (12.15 g, 36.4 mmol), potassium carbonate (5.32 g, 38.4 mmol) and potassium iodide (0.54 g, 3.3 mmol) were added while stirring. The solution was stirred at 55 °C for 3 days. The mixture was then allowed to cool to room temperature and 150 mL of distilled water added. The formed brown solid was separated by filtration and washed with hot acetone. The solid was recrystallized from 2-propanol and 6.94 g (11.3 mmol) of the product **1a** as light brown powder could be obtained.

 $\omega = 74\%$

m.p. = 74-76 °C

¹**H-NMR** (300 MHz, CDCl₃): δ(ppm) = 6.82 (s, 2H, C H_{arom}), 3.90 (t, J = 6.6 Hz, 4H, O-C H_2), 1.81-1.68 (m, 4H, O-CH₂–C H_2 –), 1.49-0.99 (m, 22H, –C H_2 –), 0.88 (t, J = 6.6 Hz, 6H, -C H_3).

¹³**C-NMR** (75 MHz, CDCl₃): δ (ppm) = 153.3 (**C**-OR), 115.5 (**C**H_{arom}), 68.8 (-O-**C**H₂-), 32.07 (-O-CH₂-**C**H₂-), 29.9-29.4 (overlapped signals, -**C**H₂-), 26.2 (-**C**H₂-), 22.8 (-**C**H₂-), 14.3 (CH₂-**C**H₃).

1.2.2 Synthesis of 1,4-Dibromo-2,4-Bis(octadecyloxy)benzene (1b)



1,4-Bis(octadecyloxy)benzene (6.94 g, 11.3 mmol) was dissolved in CH_2Cl_2 and *N*-bromosuccinimide (8.09 g, 24.8 mmol) slowly added while the solution was stirred at room temperature. The solution was stirred for 2 days and then concentrated under reduced pressure. The residue was washed with methanol, which gave rise to 8.27 g (10.6 mmol) of the desired product **1b** as a light brown powder.

 $\omega = 94 \%$

mp: 87-89 °C

¹**H-NMR** (300 MHz, CDCl₃): δ(ppm) = 7.08 (s, 2H, C H_{arom}), 3.94 (t, J = 6.6 Hz, 4H, O-C H_2), 1.84-1.71 (m, 4H, O-C H_2 -C H_2 -), 1.54-1.03 (m, 22H, -C H_2 -),0.87 (t, J = 6.6 Hz, 6H, C H_2 -C H_3).

¹³**C-NMR** (75 MHz, CDCl₃): δ (ppm) = 150.1 (**C**-OR), 118.5 (**C**H_{arom}), 111.1 (**C**-Br), 70.3 (-O-**C**H₂-), 31.9 (-O-CH₂-**C**H₂-), 29.7-29.2 (overlapped signals, -**C**H₂-), 29.1 (-**C**H₂-), 25.9 (-**C**H₂-), 22.7 (-**C**H₂-), 14.1 (CH₂-**C**H₃).

1.2.3 Synthesis of 2,5-Bis(octadecyloxy)terephthalaldehyde (1)



Under an inert gas atmosphere 1,4-dibromo-2,4-bis(octadecyloxy)benzene (**1b**, 7.53 g, 9.8 mmol) was dissolved in THF (120 mL) and the solution cooled to - 78 °C. At that temperature *n*-butyllithium (8.6 mL, 21.5 mmol, 2.2 eq) was slowly added and the solution stirred for 30 min. The solution was then allowed to warm up to room temperature and afterwards again cooled to -78 °C. DMF (1.7 mL, 21.5 mmol, 2.2 eq) was added and the reaction mixture was allowed to warm to r.t. overnight. The solution was treated with aqueous NH₄Cl solution and concentrated. The obtained solid was treated with water and the remaining solid filtered off and recrystallized in petrolether (PE). The solid was then purified by column chromatography (PE:CH₂Cl₂ 3:1 v/v, R_f = 0.1) and 1.107 g (1.64 mmol) of the desired product **1** as a light yellow powder could be obtained.

 $\omega = 17 \%$

mp: 94-98 °C

¹**H-NMR** (300 MHz, CDCl₃): δ (ppm) = 10.52 (s, 2H, C**H**O), 7.43 (s, 2H, C**H**_{arom}), 4.08 (t, J = 6.3 Hz, 4H, O-C**H**₂), 1.87-1.75 (m, 4H, O-CH₂-C**H**₂-), 1.54-1.06 (m, 22H, -C**H**₂-), 0.88 (t, J = 6.6 Hz, 6H, CH₂-C**H**₃).

¹³**C-NMR** (75 MHz, CDCl₃): δ (ppm) = 189.7 (**C**HO), 155.4 (**C**-O), 129.4(**C**-CHO), 111.8 (**C**H_{arom}), 69.4 (O-**C**H₂), 32.1 (O-CH₂–**C**H₂–), 29.8-29.2 (overlapped signals, –**C**H₂–), 26.2(–**C**H₂–), 22.9 (–**C**H₂–), 14.3 (CH₂–**C**H₃).

- 1.3 Synthesis of RC monomer
- 1.3.1 Synthesis of 1,3-Bis(octadecyloxy)benzene (2a)



To a solution of resorcinol (3.85 g, 34.9 mmol) in 150 mL of argon-purged DMF, 1–bromooctadecane (27.15g, 83.8 mmol), potassium carbonate (12.24 g, 88.5 mmol) and potassium iodide (1.24 g, 7.5 mmol) were added while stirring. The solution was stirred at 55 °C for 3 days. The mixture was then allowed to cool to room temperature and 150 mL of distilled water added. The formed brown solid was separated by filtration and washed with hot acetone. The solid was purified by column

chromatography (PE:CH₂Cl₂ 1:1, R_f =0.75) and product **2a** as a light brown powder was obtained in quantitative yield (21.50 g).

 ω = quant.

mp: 80-83 °C

¹**H-NMR** (300 MHz, CDCl₃): δ(ppm) = 7.13 (t, J = 7.8 Hz, 1H, C H_{arom}), 6.49 (s, 1H, COR–C H_{arom} –COR), 6.47 (d, J = 7.8 Hz, 2H, C H_{arom}), 3.92 (t, J = 6.6 Hz, 4H, O-C H_2), 1.82-1.71 (m, 4H, O–CH₂–C H_2 –), 1.48-1.22 (m, 22H, –C H_2 –), 0.87 (t, J = 6.6 Hz, 6H, CH₂–C H_3).

¹³**C-NMR** (75 MHz, CDCl₃): δ (ppm) = 160.4 (**C**-OR), 129.7 (**C**H_{arom}), 106.4 (**C**H_{arom}), 101.4 (**C**H_{arom}), 67.9 (O-**C**H₂), 31.9 (O-**C**H₂–), 29.7-29.2 (overlapped signals, –**C**H₂–), 26.0 (–**C**H₂–), 22.7 (–**C**H₂–), 14.2 (CH₂–**C**H₃).

1.3.2 Synthesis of 1,5-Dibromo-2,4-bis(octadecyloxy)benzene (2b)



The product 1,5-bis(octadecyloxy)benzene (27.18 g, 44.2 mmol) was dissolved in CH_2Cl_2 (200 mL) and N-bromosuccinimide (17.30 g, 97.2 mmol, 2 eq.) slowly added while the solution was stirred at room temperature. The solution was stirred for 2 days and then concentrated under reduced pressure. The residue was washed with methanol, which gave rise to 27.32 g (35.4 mmol) of the desired product **2b** as a light brown powder.

 $\omega = 80 \%$

mp: 79-81 °C

¹**H-NMR** (300 MHz, CDCl₃): δ (ppm) = 7.64 (s, 1H, CBr–C H_{arom} –CBr), 6.46 (s, 1H, COR–C H_{arom} –COR), 3.98 (t, J = 6.6 Hz, 4H, O-C H_2), 1.88-1.77 (m, 4H, O–CH₂–C H_2 –), 1.56-1.18 (m, 22H, –C H_2 –), 0.88 (t, J=6.6 Hz, 6H, CH₂–C H_3).

¹³**C-NMR** (75 MHz, CDCl₃): δ (ppm) = 155.6 (**C**-OR), 135.7 (-**C**H_{arom}-), 103.0 (**C**-Br), 99.8 (-**C**H_{arom}-), 69.7 (-O-**C**H₂-), 31.9 (O-CH₂-**C**H₂-), 29.7-29.0 (overlapped signals, -**C**H₂-), 26.0 (-**C**H₂-), 22.7 (-**C**H₂-), 14.1 (CH₂-**C**H₃).

1.3.3 Synthesis of 4,6-Bis(octadecyloxy)isophthalaldehyde (2)



Under an inert gas atmosphere 1,5-dibromo-2,4-bis(octadecyloxy)benzene (5 g, 6.5 mmol) was dissolved in THF (120 mL) and *N*,*N*,*N'*,*N'*-tetramethylethylenediamine (TMEDA, 2.9 mL, 19.4 mmol, 3 eq.) added to the solution. The solution was then cooled to - 78 °C and *n*-butyllithium (12.9 mL, 32.4 mmol, 5 eq.) was slowly added at that temperature and stirred for 30 min. The solution was then allowed to grow warm to room temperature and afterwards again cooled to - 78 °C. DMF (3.5 mL, 45.3 mmol, 7 eq.) was added and the reaction mixture was allowed to grow warm overnight. The solution was treated with aqueous NH₄Cl solution and concentrated. The obtained solid was treated with water and the remaining solid (4.17 g) filtered off. The solid (1 g) was then purified by column chromatography (PE:ethyl acetate 95:5, R_f = 0.21) and 347 mg (0.52 mmol) of the desired product **2** as a light brown powder could be obtained. Characterization of the residue of the column chromatography showed, that the also the mono-formylated compound **2d** was generated.

 $\omega = 40 \%$

mp: 89-93 °C

¹**H-NMR** (300 MHz, CDCl₃): δ(ppm) = 10.31 (s, 2H, CHO), 8.36 (s, 1H, CCHO–C*H_{arom}*–CCHO), 6.41 (s, 1H, COR–C*H_{arom}*–COR), 4.15-4.13 (m, 4H, O–C*H*₂), 1.93-1.84 (m, 4H, O–CH₂–C*H*₂–), 1.59-1.19 (m, 22H, –C*H*₂–), 0.88 (t, *J*=6.6 Hz, 6H, CH₂–C*H*₃).

¹³**C-NMR** (75 MHz, CDCl₃): δ (ppm) = 187.7 (**C**HO), 167.0 (CCHO–**C**H_{arom}–CCHO), 131.0 (**C**-O), 118.4 (**C**-CHO), 95.4 (COR–**C**H_{arom}–COR), 69.1 (O-**C**H₂), 32.9 (–**C**H₂–), 29.7-28.9 (overlapped signals, –**C**H₂–), 26.0(–**C**H₂–), 22.7(–**C**H₂–), 14.1 (CH₂-**C**H₃).

1.4 Synthesis of BP monomer

1.4.1 Synthesis of 2,2'-Bis(octadecyloxy)biphenyl (3a)



To a solution of 2,2'-biphenol (8.49 g, 45.6 mmol) in 65 mL of argon-purged DMF, 1-bromooctadecane (33.34 g, 100.0 mmol, 2.2 eq.), potassium carbonate (14.50 g, 104.9 mmol, 2.3 eq.) and potassium iodide (1.59 g, 9.6 mmol, 0.2 eq.) were added while stirring. The solution was stirred at room temperature for 3 days. The solution was then heated under reflux for 2 days and afterwards allowed to cool to room temperature. 200 mL of distilled water added and the formed solid was separated by filtration, recrystallized from 2-propanol and 31.51 g of the product **5a** as white powder could be obtained.

 ω = quant.

¹**H-NMR** (300 MHz, CDCl₃): δ (ppm) = 7.30-7.22 (m, 4H, C H_{arom}), 7.00- 6.90 (m, 4H, C H_{arom}), 3.89 (t, J=6.6 Hz, 4H, -O-C H_2), 1.66-1.53 (m, 4H, O-C H_2 -C H_2), 1.33-1.18 (m, 22H, -C H_2 -), 0.88 (t, J=6.6 Hz, 6H, C H_2 -C H_3).

¹³**C-NMR** (75 MHz, CDCl₃): δ(ppm) = 156.6 (**C**-O), 131.5 (**C**H_{arom}), 128.3 (**C**_{arom}-C_{arom}), 128.2 (**C**H_{arom}), 119.9 (-**C**H_{arom}-), 112.1 (-**C**H_{arom}-), 68.4 (-O-**C**H₂-), 31.9 (O-CH₂-**C**H₂-), 29.8-29.2 (overlapped signals, -**C**H₂-), 25.9 (-**C**H₂-), 22.7 (-**C**H₂-), 14.1 (CH₂-**C**H₃).

1.4.2 Synthesis of 5,5'-Dibromo-2,2'-Bis(octadecyloxy)biphenyl (3b)



The product 2,2'-bis(octadecyloxy)biphenyl (7.49 g, 44.1 mmol) was dissolved in CH_2Cl_2 (100 mL) and *N*-bromosuccinimide (15.69 g, 88.2 mmol, 2 eq.) slowly added while the solution was stirred at room temperature. The solution was stirred for 3 days and the reaction progress controlled via NMR. Then 2 equivalents of acetic acid (5.05 mL, 88.2 mmol) were added and the reaction stirred overnight. After again controlling the reaction progress another equivalent of *N*-bromosuccinimide (7.85 g, 44.1 mmol, 1 eq.) was added and the solution again stirred overnight. The solution was then concentrated under reduced pressure. The residue was washed with methanol, which gave rise to 24.55 g (28.9 mmol) of the desired product **5b** as a white powder.

ω = 66 %

mp: 84-85 °C

¹**H-NMR** (300 MHz, CDCl₃): δ (ppm) = 7.43-7.33 (m, 4H, -C H_{arom} -), 6.85 (d, J=9.0 Hz d, 2H, -C H_{arom} -), 3.87 (t, J=6.9 Hz, 4H, -O-C H_2), 1.66-1.52 (m, 4H, O-CH₂-C H_2 -), 1.36-1.21 (m, 22H, -C H_2 -), 0.89 (t, J=6.6 Hz, 6H, CH₂-C H_3).

¹³**C-NMR** (75 MHz, CDCl₃): δ (ppm) = 155.5 (**C**-OR), 133.9 (-**C**H_{arom}-), 131.2 (-**C**H_{arom}-), 128.7 (- **C**_{arom}-C_{arom}-), 113.6 (-**C**H_{arom}-), 112.0 (**C**-Br), 68.7 (-O-**C**H₂-), 31.9 (-O-CH₂-**C**H₂-), 29.8-29.1 (overlapped signals, -**C**H₂-), 26.0 (-**C**H₂-), 22.6 (-**C**H₂-), 14.1 (CH₂-**C**H₃).

1.4.3 Synthesis of 2,2'-Bis(octadecyloxy)biphenyl-5,5'-dicarboxaldehyde (3)



Under an inert gas atmosphere 3,3'-dibromo-2,2'-bis(octadecyloxy)biphenyl (1 g, 1.2 mmol) was dissolved in THF (50 mL) and TMEDA (0.53 mL, 3.5 mmol, 3 eq.) added to the solution. The solution was then cooled to - 78 °C and n-butyllithium (2.4 mL, 5.89 mmol, 5 eq.) was slowly added at that

temperature and stirred for 30 min. The solution was then allowed to grow warm to room temperature and afterwards again cooled to - 78 °C. DMF (0.64 mL, 8.2 mmol, 7 eq.) was added and the reaction mixture was allowed to grow warm overnight. The solution was treated with aqueous NH_4Cl solution and concentrated. The obtained solid was treated with water and the remaining solid filtered off. The solid was then purified by column chromatography (DCM, $R_f = 0.2$) and 380 mg (0.5 mmol) of the desired product **5** could be obtained as a white powder.

 $\omega = 43 \%$

mp: 99-101 °C

¹**H-NMR** (300 MHz, CDCl₃): δ(ppm) = 9.91 (s, 2H, C**H**O), 7.88 (dd, J=8.6 Hz, 1.8 Hz, 2H, C**H**_{arom}), 7.79 (d, J=1.8 Hz, 2H, C**H**_{arom}), 7.03 (d, J=8.7 Hz, C**H**_{arom}), 4.01 (t, J=6.6 Hz, 4H, -O-C**H**₂), 1.70-1.51 (m, 4H, O-CH₂–C**H**₂–), 1.34-1.15 (m, 22H, $-CH_2$ –), 0.87 (t, J=6.6 Hz, 6H, CH₂–C**H**₃).

¹³**C-NMR** (75 MHz, CDCl₃): δ(ppm) = 190.7 (**C**HO), 161.7 (**C**-OR), 133.2 (-**C**H_{arom}-), 131.7 (-**C**H_{arom}-), 129.3 (**C**-CHO), 127.4 (-**C**_{arom}-**C**_{arom}-), 111.4 (-**C**H_{arom}-), 68.6 (O-**C**H₂), 31.9 (O-CH₂-**C**H₂-), 29.8-28.9 (overlapped signals, -**C**H₂-), 25.9 (-**C**H₂-), 22.7 (-**C**H₂-), 14.1 (CH₂-**C**H₃).

1.5 Polymerization reactions

Literature protocol for the polyazine-polymers synthesis was adapted.² For bulk polymers, the dialdehyde monomer was dissolved in chloroform/ethanol mixture (3:1, v/v) and one equivalent of hydrazine was added as ethanolic solution, the mixture was refluxed for 3 days. Then the solvent was removed on a rotary evaporator and the polymer was obtained as a solid. For NMR experiments, 0.5 mL of 20 mM solution of the dialdehyde monomer in CDCl₃ was mixed with 10 μ L of 1 M hydrazine solution in d₄-methanol and heated at 50 °C in sealed tube. The reaction was observed at given time intervals by NMR spectroscopy. Polycondensations with *p*-phenylenediamine were performed in pure chloroform as a solvent since both reactants are readily soluble in it, but the reaction times were extended to 5 days in these cases.

The reaction rate can be accelerated by addition of *n*-propylamine. The action principle of primary amine catalysis has been already realized in previous instances.^{3,4} In brief, aliphatic amines are kinetically faster in reactions with aldehydes, however the thermodynamically favored product is the hydrazone or conjugated polyimine for reactions involving hydrazine or *p*-phenylenediamine, respectively. Also, imine exchange reactions proceed much faster than the condensation counterparts, thus addition of primary aliphatic amines accelerates the polyazine formation. Finally, *n*-propylamine is a volatile compound with low boiling point and is thus easily removed on the rotary evaporator.

On-surface polymer growth was performed from chloroform solutions at a given dialdehyde monomer concentration (typically 50 μ M, if not explicitly stated otherwise) into which graphene on a Si/SiO₂ wafer was immersed for 30 minutes. After the pre-equilibration period, 1 eq. of the diamine was added, solution was stirred quickly and let undisturbed overnight (approx. 12 hours), then removed and quick immersed into clean chloroform and dried in a stream of argon. The overnight polymerization can be eventually shorter, however in some case unfinished growth on some parts of the sample was observed after 2 hours reaction, thus 12 hours was typically used.

2 Chemical vapor deposition (CVD) of graphene

Graphene was grown on copper using the CVD method.⁵ Polycrystalline copper foil was annealed at a hydrogen flow of 50 sccm at T = 1000 °C for 20 minutes, which is when the methane precursor was introduced into the chamber with a flow of 1 sccm. The process was carried out for 30 minutes under a pressure of 350 mTorr. Then, CH_4 gas was switched off and the sample remained in the presence of the flow of H₂ gas for 5 minutes to etch the top layer. Next, the sample was cooled to room temperature under a continuous flow of hydrogen. Transfer to a Si/SiO₂ wafer substrate was performed using the polymer-assisted (nitrocellulose) copper etching (FeCl₃) technique.⁶

2.1 Fabrication of graphene stripes

CVD graphene on Si/SiO₂ substrate was covered with photoresist AZ 6632 by spin-coating, aligned with the mask, exposed to the mercury short arc lamp light and developed with its own developer (AZ726MIF). Then graphene was etched by oxygen plasma and the polymer mask was removed by acetone. Samples were then washed with 2-propanol and dried under a nitrogen flow. The size of the graphene stripes was ranging from 3 to 20 μ m.

3 UV-Vis and PL spectroscopy

3.1 General

UV-Vis characterizations were carried out with a UV-Vis-NIR spectrometer Perkin-Elmer Lambda 1050 in a quartz-cuvette and baseline corrected. Sample and reference were measured simultaneously.

Photoluminescence experiments were recorded on HORIBA Jobin-Yvon Fluorolog 3 with a 450 W xenon lamp or KOHERAS Supercontinuum Laser in quartz-cuvettes or on silica-substrates and with a R928 photomultiplier as detector. Fluorescent pictures were recorded with the inverted Olympus BX microscope connected to the CCD camera.

3.2 UV-Vis spectra



Figure S 2 Normalized UV-vis spectra of the three monomers and the six polymers (HQ – blue, RC – red, BP – green). Spectra measured in chloroform at concentration of about 0.3 mg/mL. In all cases either shift or new absorbance features at longer wavelengths are observed. The red-shifted absorbance is attributed to the extended conjugation caused by the conjugated dynamer formation.

Table S 1 Data summary for the most red-shifted absorbance feature in the UV-vis spectra of the considered dialdehyde monomers **HQ**, **RC**, **BP** and their polymers with **hd** or **pp**. Clear shift towards longer wavelengths is observed upon polymer formation in all cases, attributed to the extended conjugation. Only the most red-shifted features are listed for clarity, all values are given in nm.

Absorbance maxima	Dialdehyde monomer	Polymer with hd	Polymer with pp
HQ	400	425	430
RC	289	330	380
BP	281	355	381

3.3 PL spectra



Figure S 3 Acquired emission spectra of the 6 polymers and monomers (HQ – blue, RC – red, BP – green) measured in chloroform solution at concentration of about 0.03 mg/mL. Excitation wavelengths: HQ – 427 nm, RC – 327 nm, BP – 358 nm. In all cases, very broad emission extending the one of the monomer is observed. We attribute this to the extended conjugation upon dynamer formation together with the inherent polydispersity of the dynamer chain lengths. Spectra are normalized (except for RC-monomer).

Table S 2 Summary of the PL emission data for monomers the thereof polymers. N/A = no emission detected (in CHCl₃, nM to mM concentration range). * = extremely broad emission, actual very shallow maxima were identified by curve fitting at 439 and 571 nm. ^{\$} multiple features at different wavelengths, please inspect the actual PL spectra. All values are given in nm, only the most red-shifted emission features are listed for clarity.

Emission maxima	Dialdehyde monomer	Polymer with hd	Polymer with pp
HQ	473	475	526
RC	N/A	430-650*	380
BP	403 ^{\$}	431 ^{\$}	431 ^{\$}

PL spectroscopy showed two different scenarios, either a) the emission peak maximum was redshifted upon polymer formation vs. the dialdehyde monomer, or b) the emission maximum position was preserved, but its "tailing" towards longer wavelengths was strongly enhanced upon polymer formation. These cases can be clearly attributed *ad a*) to the extended π -conjugated system being formed, or *ad b*) a polydisperse mixture of species with different conjugation lengths. In general, polydispersity of the dynamer chain lengths must always be considered.



Figure S 4 Absorbance, excitation and emission spectra of **HQ:hd** dropcasted film on quartz. The polymer was prepared in bulk, dissolved in chloroform and dropcasted on a quartz slide. Upon evaporation, a film on the airliquid interface was formed and then the residual underlying solution was removed by an edge contact with a paper tissue. In this way, **HQ:hd** film was homogeneously covering most of the quartz slide, which was not possible to achieve by other methods. The absorbance spectrum was measured a 60 mm spectralon integration sphere in a diffuse transmittance configuration.

4 Raman spectroscopy

4.1 General

Raman spectra were acquired with the WITec alpha 300 R (WITec GmbH) with confocal microscope (50x and 100x vis LWD lenses), and 532 nm excitation wavelength, or LabRAM HR (HORIBA Jobin-Yvon), with Olympus BX microscope, 50x and 100x vis LWD lenses, excited by 633 nm wavelength. Excitation profiling was also performed on LabRAM HR using the Coherent Innova 70C Spectrum tunable laser source for 457, 476, 488, 514, 531, 568, 647 nm excitation and 633 He-Ne laser. All band positions were fitted with pseudo-Voigt line shape.



4.2 Raman spectra of polymers and their films on graphene

Figure S 5 Recorded Raman spectra of the polymers on glass excited with 532 nm laser line. A) Raman spectrum of the **HQ:hd** polymer on glass slide showing three dominant features 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 symmetric C=C stretching vibration, respectively. The peak at around 1000 cm⁻¹ is due to the glass substrate. The sharp signal of CH₂ twisting vibrations indicates high level of crystallinity.⁷ B) Raman spectra of other polymers prepared. **RC:pp** spectrum was totally dominated by PL and is thus not listed. Significant broadening of the CH₂ twisting mode is observed as a result of decreased layer crystallinity.

The polymers were deposited on glass by drop-casting the chloroform solution and Raman spectra recorded (displayed in Figure S 5). Figure S 5 shows only five spectra, due to the fact that the photoluminescence of the **RC:pp** polymer was superposing the Raman signals. Photoluminescence was also detected for the five other polymers, but also Raman signals could be observed. Figure S 5A displays the obtained Raman spectrum for **HQ:hd** polymer. The observed Raman spectra can be divided into two structural fragments and described using corresponding literature data:

- A) The aliphatic side chains can be regarded as "lipids" or polyethylene fragments for which the CH₂ twisting vibration is typically observed at around 1300 cm⁻¹ if *trans* conformation prevails.^{7,8} Sharp peak at lower wavenumbers is indicative of very high crystallinity of the aliphatic chains, whereas amorphization leads to shift towards higher wavenumbers and dramatic signal broadening. In our series, the sharpest peak is observed for HQ:hd at 1293 cm⁻¹ indicating very high level of film crystallinity. In comparison, HQ:pp and RC:hd spectra show much broader signal over 1300 cm⁻¹ suggesting more vague organization and for BP this band in thin film is so broad that it cannot be distinguished from the background as a result of totally amorphous material.
- B) The conjugated backbone on the other hand has resemblance to poly(phenylene vinylene) (PPV) which can be used to understand the observed spectra.⁹ In the PPV spectrum, different Raman shift is observed for the vinylic and ring C=C stretch vibrations (1545 and 1582 cm⁻¹, respectively) which is further dependent on the level of doping in the system. In the HQ:hd case, the "vinylic" part is replaced by the C=N–N=C azine vibration which due to the higher mass of N vs. C shifts the vibration to lower wavenumbers (1525 cm⁻¹). Similar band is found also in RC:hd (1545 cm⁻¹) and BP:hd (1555 cm⁻¹), but is not observed for pp–based polymers. The ring C=C vibrations in PPV are downshifting to 1568 cm⁻¹ when potential applied as a result of doping. In HQ:hd, this vibration is found at 1573 cm⁻¹ which might be due to inherent doping by heteroatoms and at 1585 cm⁻¹ for all other hd-polymers in the series. For pp-based polymers this band splits to doublet, presumably due to presence of two distinct aromatic cores. Additional bands at around 1150 cm⁻¹ are found in the pp-based materials assigned to the ring vibration of *p*-disubstitued benzene.



Figure S 6 Raman Spectra of the polymers on graphene on Si/SiO_2 substrate excited with 532 nm laser line. Left: **HQ:hd** polymer on CVD graphene with concomitant signal originating from the polymer (1295, 1525 and 1575 cm⁻¹, assignment is given above) and graphene (1600 and 2700 cm⁻¹ for G and 2D mode respectively), the signal at around 1000 cm⁻¹ is due to the substrate. Right: spectra of the other polymer in the investigated series on CVD graphene. Spectra are analogous combining features of pristine polymers and pristine graphene. The spectrum of **RC:pp** is also provided because graphene quenches the strong luminescence overwhelming the spectrum of the polymer alone, as observed also in previous studies.

4.3 Raman excitation profile



Figure S 7 Raman excitation profile of **HQ:hd** polymer on graphene in the range from 458 to 647 nm. Excitation at 458 and 488 nm gives also bands attributed to the C-H stretch vibrations and overtones, excitation at 633 or 647 nm yields very weak spectra making the Raman mapping time consuming. Ideal compromise was found around 532 nm.



Figure S 8 Intensity of Raman scattering for the selected peaks at different excitation wavelengths. 1 mW excitation laser intensity on the sample, 30 s integration, 2 accumulations, 100x objective, 600 g/mm grating.

4.4 Strain-doping analysis from Raman mapping

Raman maps were recorded at the edges of graphene with epitaxially grown **HQ:hd** and **HQ:pp** polymer layers on graphene (~5 nm thickness). Fitting of the polymer signals at 1293, 1525 and 1570 cm⁻¹ signals as well as graphene G and 2D modes at around 1600 and 2700 cm⁻¹ show full colocalization. Moreover, from the positions of the graphene's mode, the ω_G , ω_{2D} plots can be calculated and the mechanical strain and doping levels in each point can be derived according to the published method.¹⁰ In general, the mechanical strain in our samples is negligible at around -0.02 % (compressive strain) and does not change when the polymer layer is grown on graphene. The doping in pristine graphene was found at around 13.5 x 10¹² cm⁻² but when **HQ:hd** or **HQ:pp** polymer layer is formed on top of it, it drops by about 30 % to 9.66 or 9.98 x 10¹² cm⁻², respectively. We attribute this to the compensation of the substrate induced p-doping (p⁺⁺ Si).



Figure S 9 Strain (a) and doping (b) analysis from fitted Raman map of the pristine CVD graphene transferred onto Si/SiO₂ (p++ silicon) via polymer assisted method. Relatively high doping (1.35 x 10^{13} cm⁻¹) is due to the interaction with the substrate. Only very small compressive strain (-0.01 %) is observed.



Figure S 10 Strain (a) and doping (b) distribution from Raman map fitting of **HQ:hd** spincoated on graphene. Only negligible difference in strain is observed as compared to pristine graphene, however the doping after **HQ:hd** deposition was decreased by about 30 %. c) Optical image with the mapped area indicated in green, parts without graphene or with graphene multilayers were omitted from analysis.



Figure S 11 Strain (a) and doping (b) distribution from Raman map fitting of **HQ:pp** spincoated on graphene. Only negligible difference in strain is observed as compared with pristine graphene, however the doping was decreased by about 30 %, similarly to **HQ:hd** case. c) Optical image with the mapped area indicated in green, parts without graphene or with graphene multilayers were omitted from analysis.

5 X-ray photoemission spectroscopy

The XPS spectra of the samples were measured using a SPECS electron spectrometer equipped with a hemispherical Phoibos 150 electron analyser operated in a fixed transmission mode. Al K α monochromatized radiation was used for electron excitation. The binding energy scale was calibrated using the Au $4f_{7/2}$ (84.0 eV) and Cu $2p_{3/2}$ (932.6 eV) photoemission lines. Binding energy steps were 0.1 eV with 200 ms dwell time per step. The pressure in the XPS analysis chamber during spectra acquisition was 4×10^{-10} mbar. The spectra were collected at a detection angle of 90° with respect to the macroscopic surface of the sample. Survey scan spectrum and high-resolution spectra of N 1*s*, C 1*s* and O 1*s* photoelectrons were measured. The accuracy of the measured binding energies was ±0.1 eV. To get more details on the chemical states of the present elements the spectra were curve fitted after subtraction of Shirley background¹¹ using the Gaussian–Lorentzian line shape and non-linear least-squares algorithms (software CasaXPS ver. 2.3.15 and XPSPEAK 4.1).* For graphitic sp² carbon component asymmetric line shape was used.

^{*} A freeware program written by R.W.M. Kwok, Dept. of Chemistry, University of Hon Kong, Shatin, Hong Kong. Software can be downloaded from http://xpspeak.software.informer.com/4.1/



Figure S 12 XPS survey scan (a) and fitted spectrum of C 1s photoelectrons (b) of freshly cleaved HOPG substrate free of contaminants. Only one asymmetric component at 284.4 eV accompanied with satellite separated by 6.2 eV from the main line characteristic of sp^2 carbon are present.



Figure S 13 X-ray photoelectron spectra of the **HQ:hd** polymer layer grown on HOPG. a) survey scan, b) fitted spectrum of C 1s photoelectrons. The low binding (284.4 eV) asymmetric component corresponds to contribution from graphite, component centered at 285.2 eV belongs to carbon atoms in hydrocarbon chains and minor component at 286.5 eV is assignable to carbon atoms in C-O and C=N bonds. c) spectrum of N 1s photoelectrons presents one main peak at 399.5 eV attributed to nitrogen in –C=N-N=C- bridges, less intense components centered at 401.2 and 403.0 eV are consistent with presence of nitrogen in C-NH and C=N-O functionalities. The binding energies of the latter two components agree within experimental error with those observed with sample of HOPG after its interaction with chloroform solution of hydrazine (see Fig. S16)



Figure S 14 X-ray photoelectron spectra of the **HQ:hd** polymer layer on HOPG prepared by drop casting of polymer solution in chloroform. The thickness of the layer estimated from attenuation of C 1s sp² component intensity assuming inelastic mean free path of photoelectrons in the layer 3.5 nm is 4.8 nm. For assignment of spectra components see caption to Fig. S14. Stoichiometry of the layer determined from integrated intensities of C 1s, N 1s and O 1s spectra after subtraction of Shirley and contribution from graphite C 1s component was determined to be $C_{44.0}N_{1.9}O_{2.5}$, which is close to the expected stoichiometry of the polymer.



Figure S 15 XPS spectra of HOPG substrate exposed to hydrazine solution. The two weak N 1s signals at 401 and 403 eV originate likely from hydrazide moieties formed at HOPG defects and layer edges and these signals are commonly found in all previous samples containing hydrazine.

6 Scanning tunneling microscopy

Scanning Tunneling Microscopy (STM) measurements were carried out on a Nanoscope Multimode 8 with A-scanner and standard STM scanning head at room temperature using a mechanically cut Pt/Ir tip. All solution samples (6 μ L) were applied onto the basal (0001) plane of freshly cleaved HOPG. The self-assembled molecular network (SAMN) was visualized by STM using constant current mode at the liquid/solid interface. Molecular resolution was achieved at positive tip biases. Image analysis and calibration was performed using WSxM software.¹²



Figure S 16 UV-Vis absorption spectrum of **HQ** monomer, the reaction mixture applied for on-surface polymer growth and ex-situ synthesized **HQ:hd** polymer. Upon mixing **HQ** and **hd** with a catalytic amount of octanoic acid (0.1% v/v), the mixture showed a significant increase of λ_{max} (~410 nm) and a redshift (~30nm) of the adsorption peak, as compared to **HQ** monomer. These changes strongly indicate the polymerization has started.



Figure S 17 A survey of **HQ** self-assembly at the TCB/HOPG interface with a gradual increase of **HQ** concentration in TCB solutions. Some minor phases were observed occasionally at 0.8 mM and 0.9 mM, but they diminished quickly after one scanning frame. The stable **HQ** self-assembly was observed only starting from 1 mM.



Figure S 18 Two consecutive STM images of (a) the HQ self-assembled monolayer at 1 mM concentration and (b) the underlying HOPG substrate. (c) The image merged from (a) and (b). (d) The autocorrelation of STM image (c). The black arrows indicate the unit cell vectors of the molecular superstructure, and the red arrows indicate the unit cell vectors of the underlying HOPG lattice.

The HQ monolayer structure exhibits a definite epitaxial relationship with the underlying HOPG substrate. The unit cell vector \vec{a} (0.852 nm) of the molecular overlayer is rotated with respect to the unit cell vector $\vec{a_1}$ (0.246 nm) of HOPG lattice by 30° and the \vec{b} (2.918 nm) is rotated by 9.059° with respect to the other $\vec{a_2}$ (0.246 nm) as demonstrated in the autocorrelation of the image (Figure S 18d). Expressing the unit cell of the molecular overlayer in matrix form yields:

$$\begin{pmatrix} \mathbf{a} \\ b \end{pmatrix} = \begin{pmatrix} \mathbf{4} & -\mathbf{2} \\ \mathbf{2} & \mathbf{11} \end{pmatrix} \begin{pmatrix} a_1 \\ a_2 \end{pmatrix}$$



Figure S 19 a-b) STM images of in-situ polymerization of **HQ** and **pp** at the TCB/HOPG interface showing multioriented small domain of lamellar structures. c) Proposed molecular model of **HQ:pp** polymer assembly superimposed on STM image cut from (b). d-e) STM images of in-situ polymerization of **RC** and **hd** at the TCB/HOPG interface showing multi-oriented small domain of lamellar structures. f) Proposed molecular model of **RC:hd** polymer assembly superimposed on STM image cut from (f).

The quality of CVD grown graphene transferred onto Si/SiO_2 substrates was also examined by STM imaging, which shows characteristic HOPG-like honeycomb lattices as revealed by both STM topography and 2D-FFT analysis (Figure S 20 and onset). The variation of the image contrast and lattice distortion indicate a curved surface, which might be due to graphene wrinkling during the transfer.



Figure S 20 a-b) STM images and 2D-FFT analysis (onset) of CVD grown graphene transferred onto Si/SiO_2 substrate.



Figure S 21 a-c) STM images of in-situ grown **HQ:hd** polymers on CVD grown graphene transferred onto Si/SiO₂ substrate.

7 Diffusion NMR spectroscopy

NMR diffusion measurements were carried out on Bruker Avance IIIHD spectrometer operating at magnetic field of 11.75 T (500.45 ¹H resonance frequency) equipped with GREAT60 magnetic field gradient amplifier, Micro5 probe head body, diff50 *z*-gradient coil and 5 mm double radio frequency coil tuned for ¹H and ²H, thus allowing a field-frequency lock. The diffusion spectra were acquired with the double stimulated echo pulse sequence¹³ to compensate for convection artifacts.

Samples of polymer and monomer were dissolved in CDCl₃ (EurisoTOP) at concentration of 10 mg/mL and they were placed into 5 mm Shigemi tubes with susceptibility matched to chloroform so that sample height was about 8 mm. The spectra were acquired at temperature 298.2 K using the double stimulated echo pulse sequence.¹³ Two values of the total diffusion time (20 ms and 60 ms) were used in order to verify that convection is not affecting the results. The gradient was incremented linearly in 32 steps between minimum value (0.114 T/m and 0.07 T/m, respectively) and the maximum value (3.28 T/m and 1.89 T/m, respectively), the diffusion encoding gradient pulses were

of sine bell shape with 1 ms duration. The pulse sequence involved 5 ms longitudinal eddy current delay, spoiling gradients were applied in all three periods when the wanted magnetization was stored along z-axis, a spoiling sequence was also used prior to each scan, the repetition time was 5 s and 90 deg radiofrequency pulse was 8.2 μ s. The peak integrals dependences on the gradient strength were fitted to the Stejskal-Tanner equation modified for the double stimulated echo¹³ within the spectrometer software (Topspin 3.2).

The ¹H NMR spectrum of the **HQ:hd** mixture of different species after polymerization displays 3 well separated peaks that have been assigned to the oligomer. The signal decays were mono exponential with respect to the squares gradient strength and the diffusion coefficient obtained from the spectra acquired with two different values of diffusion time (20 ms and 60 ms) was identical within the experimental standard error (4%, standard deviation of 6 obtained values). The average value of the diffusion coefficient of the oligomer is 2.75×10^{-10} m² s⁻¹. The diffusion coefficient of 5.43×10^{-10} m² s⁻¹ of the **HQ** monomer was determined in the same way as that of the oligomer, in order to obtain a reference value. According to the Stokes-Einstein equation, the diffusion coefficient is inversely proportional to the hydrodynamic radius of a spherical particle.



Figure S 22 Kinetics of the polycondenstion reaction between HQ and hd measured in CDCl₃ by NMR at 20 mM concentration of both reactants at 25 °C. Time axis is in logarithmic scale for clarity, equilibrium is reached in about 6 days. Mono-aldehyde indicate HQ with only one CHO group converted to the hydrazone, mono-hydrazone indicates CH=N-NH₂ group, azine stands for CH=N-N=CH group.

8 GPC analysis

GPC analysis was performed on Agilent Infinity II 1260 chromatograph equipped with PLgel 5µm MIXED-C column, variable wavelength UV-vis detector, dual angle light scattering (90° and 15°) and refractive index detector (all Agilent).

The system was calibrated using narrow polydispersity polystyrene standards (EasyVials, Agilent) with molecular weights in the range of 0.6 to 360 kDa. Light scattering detector calibration was performed on a peak which had the closest elution time as compared with the **HQ:hd** analyte. 20 μ L of a polymer stock solution at the concentration of 1 mg/mL in chloroform was injected on the column at flow of 1.00 mL/min and the analysis was performed for 15 minutes. The chromatogram is shown in Figure S 23 and the result of light-scattering analysis is shown in Figure S 24. Relatively broad peak with several shallow maxima is obtained and the light-scattering revealed dominant mass

of about 5 kDa in good agreement with the elution time. This mass corresponds approximately to 7mer, however shorter oligomers are also observed both in chromatogram and molecular weight distribution diagram. This shorter species can originate either from the equilibrium constitution of the mixture of from fractionation and re-distribution of oligomers during the separation.



Figure S 23 GPC chromatogram of **HQ:hd** with traces from UV-vis, refractive index and dual angle light scattering detectors. Calculated MW line is also shown. The dominant peak at around 8 minutes exhibits several shallow maxima roughly corresponding to the monomer mass difference.



Figure S 24 Results of light-scattering analysis with molecular mass distribution. Major mass is found at around 5 kDa corresponding to approximately 7-mer, other signals roughly correspond to shorter oligomers. Apparent polydispersity index of 2.27 indicates re-equilibration of the dynamer on the GPC column.

9 Graphene-polymer heterostructures

9.1 Prepared by spincoating

All polymers have been spincoated from 0.3 g/mL solutions in $CHCl_3$. Please note that CH_2Cl_2 is not a feasible substitute in this case since the polymers are insoluble in dichloromethane.

Table S 3 Optical microscopy and Raman spectroscopy investigation of the hybrid graphene:polymer heterostructure film formation. In all cases, the Raman signals of the polymer and graphene 2D mode are colocalized. For the polymer mapping, signal at around 1300 cm⁻¹ well separated from the graphene signals was used (Figure S 6). Similarly, the 2D mode was used because the G peak overlaps with some polymer signals. Graphene ruptures and folds are only due to the edge effects.

Polymer	Optical image of the recorded area	Polymer signals	Graphene 2D mode
HQ:hd	9 µm	3 μπ	3 100
HQ:pp		300	3 MR
RC:hd	9 gm		
RC:pp	9 ym		410
BP:hd	Bum		4 97
ВР:рр	9 um	4 μπ	4 um

9.2 On-surface growth of HQ:hd

Formation of the highly order dynamer layer on graphene observed by STM is a thermodynamic process at equilibrium between the on-surface layer formation and the liquid phase. It is thus

important to determine the critical concentration at which the prepared layer becomes unstable due to high dilution, which for the **HQ:hd** case was found to be at about 1 pM (Table S 4). The concentration was varied over nine orders of magnitude, the stock solutions were prepared as 100 mM and then subsequently diluted to the final concentrations.

Table S 4 Optical microscopy and Raman spectroscopy investigation of the **HQ:hd** growth on the graphene surface at various concentration. The volume was fixed at 25 mL, graphene sheet area is always about 1 cm². Spectra measured on dry films on graphene.

Concentration	Optical image of the recorded area	Polymer signals	Graphene 2D mode
1 mM	Bum	4 ym	No fit possible due to background caused by photoluminescence (Figure S 25)
1 μΜ		4 gm	4 µm
1 nM	- Gym	-4 Jar	- A fam
1 pM	3100		



Figure S 25 Raman spectrum of the on-surface grown **HQ:hd** polymer on graphene on silica substrate from 1 mM solution. Strong luminesce at around 620 nm (2700 cm⁻¹). The luminescence is due to relatively thick film formation (see AFM below) and thus non-efficient luminescence quenching by graphene.

Table S 5 Atomic Force Microscopy (AFM) measurements were carried out at room temperature with AFM Dimension Icon (Bruker) in peak force mode.

Concentration	Image of Height Topography	Height Profiles	Average Height



10 References

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