

# Printing Chemistry

# Microcontact Printing Patterning of an HOPG Surface by an Inverse Electron Demand Diels-Alder Reaction

Jun Zhu, Jonathan Hiltz, Ushula M. Tefashe, Janine Mauzeroll, and R. Bruce Lennox<sup>\*[a]</sup>

**Abstract:** The chemical modification of an sp<sup>2</sup> hybridized carbon surface in a controllable manner is very challenging but also crucial for many applications. An inverse electron demand Diels–Alder (IEDDA) reaction using microcontact printing technique is introduced to spatially control the modification of a highly ordered pyrolytic graphite (HOPG)

#### Introduction

Graphene has a number of fascinating electric, thermal, and mechanical properties.<sup>[1-4]</sup> The chemical or physical modification of the highly inert sp<sup>2</sup> surface of graphene provides an entry into the controlled modulation of these properties and/ or the ability to interface graphene to materials and devices. Covalent modification strategies provide control over the extent of the surface reactions, site specificity of modification, precise product formation, and robustness to subsequent chemical modification/degradation. The most commonly used method for the covalent modification of graphene or graphite requires harsh reaction conditions (e.g., concentrated nitric/sulfuric acid) or highly reactive reagents, such as those involved in prolonged heating/photo-irradiation associated with diazonium radical chemistry.<sup>[5,6]</sup> A mild, catalysis free, and rapid covalent modification method for graphene is thus much sought after.

Only a limited number of studies involving Diels–Alder reactions on graphite and graphene have been reported, even though these sp<sup>2</sup> hybridized carbon materials can serve as either as a dienophile or a diene.<sup>[7–10]</sup> For example, Haddon and co-workers showed that graphite/graphene can serve as a diene by reacting with tetracyanoethylene (TCNE) at room temperature. It can also serve as a dienophile, as in the reaction with 2,3-dimethyl-1,3-butadiene (50 °C, 3 h).<sup>[8]</sup> Wan and coworkers demonstrated that graphene can react with a sterically strained *cis*-diene leading to surface modifications.<sup>[7]</sup> The Braunschweig group showed that cyclopentadiene can covalently react with a graphene surface under high pressure

 [a] Dr. J. Zhu, Dr. J. Hiltz, Dr. U. M. Tefashe, Prof. J. Mauzeroll, Prof. R. B. Lennox Department of Chemistry McGill University
801 Sherbrooke St. West, Montreal, QC H3A 2K6 (Canada) E-mail: bruce.lennox@mcgill.ca

Supporting information and the ORCID number(s) for the author(s) of this
article can be found under https://doi.org/10.1002/chem.201801326.

Chem. Eur. J. 2018, 24, 1-7

surface under ambient conditions. The covalent modification was characterized by Raman spectroscopy, XPS, and SECM. Tetrazine derivatives can effectively react with an HOPG surface and with microcontact printing methods resulting in spatially patterned surfaces being produced with micrometer-scale resolution.

Diels-Alder conditions.<sup>[9]</sup> A patterned surface is subsequently produced by dip-pen lithography using this process.<sup>[9]</sup> More recently, Simon and co-workers demonstrated the direct visualization of the covalent cycloaddition of maleimide derivatives on the defect-free basal graphene plane by scanning tunneling microscopy.<sup>[10]</sup>

Inverse electron demand Diels–Alder reactions (IEDDA) have been the subject of considerable interest in biorthogonal conjugations.<sup>[11]</sup> The Fox and Weissleder research groups independently introduced the IEDDA reactions between a 1,2,4,5tetrazine and strained dieneophiles as a highly efficient method for biomolecules.<sup>[12,13]</sup> The application of IEDDA for bioorthogonal coupling has expanded quickly due to its fast reaction kinetics ( $k_2 = 2000-22000 \text{ m}^{-1} \text{ s}^{-1}$ ) and catalysis-free coupling conditions.<sup>[14]</sup> Beckmann et al. have applied the IEDDA reaction for surface modifications on tetrazine-derivatized glass slides, which can react with dienophile tethered functional carbonhydrates using an auto-array printer.<sup>[15]</sup>

Microcontact printing is a well-established means to prepare patterned surfaces due to the facile fabrication of the requisite master stamps and the compatibility of the ink and stamping method with many substrates.<sup>[16,17]</sup> Roling et al. applied the microcontact printing method together with an IEDDA reaction to introduce a tetrazine-terminated atom-transfer radical polymerization (ATRP) initiator onto an alkene terminated glass surface.<sup>[18]</sup> Polymers containing a variety of functionalities can be introduced on to the patterned surface thereafter. However, to the best of our knowledge, the IEDDA reaction has not been applied to the preparation of patterned covalently modified sp<sup>2</sup> hybridized carbon surfaces. We recently reported the use of an IEDDA reaction to modify single-wall carbon nanotubes and highly ordered pyrolytic graphite (HOPG) surfaces with tetrazine-derivatives and tetrazine-terminated gold nanoparticles (tetrazine-AuNP).<sup>[19-21]</sup> In these examples, the IEDDA reaction was carried out under ambient conditions (room temperature, atmosphere pressure) followed by a rapid retro-Diels-Alder reaction to generate the final cycloaddition adducts. Here, we

Wiley Online Library



demonstrate the site-specific covalent modification of an HOPG surface using microcontact printing delivery of IEDDA reagents. A patterned PDMS stamp thus "inked" with tetrazine derivatives generates a covalently modified HOPG surface (Scheme 1). The covalent modification of an HOPG surface was



**Scheme 1.** Schematic of the process of microcontact printing of HOPG by IEDDA covalent modification. (a) Microcontact print using ferrocene-tetrazine (Fc-O-Tz). Scale bar 200  $\mu$ m. (b) Synthesis of ferrocene-tetrazine (Fc-O-Tz) ink.

carried out at ambient conditions and characterized by Raman spectroscopy and X-ray photoelectron spectroscopy (XPS). The continuity and integrity of the conductivity of the resulting patterned surface features were determined by scanning electrochemical microscopy (SECM). The SECM technique provides spatially resolved surface reactivity information with micrometer level resolution.<sup>[22,23]</sup> A significant advantage of the tetrazine IEDDA chemistry used here is the accessible nature of the mono- or di- derivatization of dichlorotetrazine with thiol- or hydroxyl-containing molecules. Due to the higher strain and greater steric hindrance of HOPG versus graphene, reactions successfully performed on graphite/HOPG are likely to be applicable to graphene as well.<sup>[24-27]</sup>

#### **Results and Discussion**

The ferrocene-derivatized tetrazine (Fc-O-Tz) was synthesized by reacting 3,6-dichlorotetrazine with ferrocenemethanol following a previously published procedure (Scheme 1).<sup>[18]</sup> The microcontact printing stamps were prepared from a polydimethylsiloxane silicon elastomer (PDMS, Sylgard 184, Dow Corning). The PDMS master stamp was prepared following the published standard thermal crosslinking method.[28] Fc-O-Tz ink (1 mg mL<sup>-1</sup>, in anhydrous DCM) was dropcast onto the PDMS stamp. After evaporating the solvent for 1 min, the stamp was applied to a fresh prepared HOPG surface (by exfoliation/peeling) and a force of  $10 \text{ g cm}^{-2}$  applied to the stamp for 5 min. The HOPG surface was then washed with copious amounts of ethanol and dichloromethane until no unreacted tetrazine derivatives were detected in the waste wash. As shown in Scheme 1, square features with dimensions of  $150 \times 150 \,\mu\text{m}^2$ are formed on HOPG as revealed by optical microscopy imaging. Control experiments using ferrocenemethanol, which is not expected bind to HOPG, were also carried out using the same printing and washing conditions. No residual ferrocenemethanol was detected on the HOPG surface after washing. Linear Raman spectroscopy measurements were performed to determine the spatial resolution of the microcontact printing method as used here.

The outcome of the IEDDA reaction between HOPG and Fc-O-Tz was assessed using Raman spectroscopy (Figure 1). Spectra obtained (633 nm line of a HeNe laser, 4 mW power using a  $100 \times$  microscope objective) at different areas on the unmodified surface are similar to that of the pristine HOPG; a characteristic G band and 2D band at  $1579 \text{ cm}^{-1}$  and  $2680 \text{ cm}^{-1}$ , respectively (Figure 1a). Spectra collected at different areas on the modified surface are statistically consistent with there being a uniform modification of the pattern area on the HOPG surface (Figure 1b). The formation of the Fc-O-Tz adduct with HOPG is readily established by comparing the Raman spectra of (a) HOPG, (b) Raman spectra on (Fc-O-Tz-HOPG) and off (pristine HOPG) the modified HOPG surface, and (c) Fc-O-Tz. A



**Figure 1.** Raman spectra of Fc-O-Tz on a microcontact-modified HOPG surface. (a) Unmodified HOPG surface; (b) overlay of the Raman spectra on and off the modified HOPG surface; (c) Fc-O-Tz;(d) Raman spectra were collected at 3  $\mu$ m intervals along the scan direction of a 10  $\mu$ m wide stripe-pattern. The sharp increase and drop of the Raman intensity along the scan direction indicates a pattern resolution in micrometer dimension. The characteristic G band, 2D band of HOPG, and D bands due to the IEDDA adducts are high-lighted.

Chem. Eur. J. 2018, 24, 1 – 7 www.chemeurj.org

© 2018 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

2



D band observed at 1340 cm<sup>-1</sup> is attributed to the breathing vibration mode of the sp<sup>2</sup> carbon ring which becomes Ramanactive when the nearby lattice symmetry changes, as in the conversion of sp<sup>2</sup> carbon to sp<sup>3</sup> carbon. As expected, the Diels-Alder reaction of tetrazine derivatives with the HOPG surface introduces sp<sup>3</sup> carbons, leading to an increase of the D band intensity. Because the D band (at 1340 cm<sup>-1</sup>) and G band (at 1580 cm<sup>-1</sup>) merge with the tetrazine adduct ring mode at 1385 and 1522 cm<sup>-1</sup> respectively, it was not possible to accurately determine the  $I_D/I_G$  ratio. However, introducing the Raman active cyclopentadiene groups (CP) from ferrocene improves the ability to monitor the formation of the Diels-Alder adducts. The large multiplets (associated with the cylclopentadiene ring) observed between 550-600 cm<sup>-1</sup> are attributed to the cyclopentadiene ring tilting and deformation modes. The detailed Raman assignments are summarized in Table 1.

| Table 1. Assignment of Raman bands of Fc-O-Tz on HOPG. |                                     |
|--|-------------------------------------|
| Raman Shift<br>[cm <sup>-1</sup> ]                     | Vibration Mode                      |
| 1340   | HOPG D band                         |
| 1580   | HOPG G band                         |
| 2685   | HOPG 2D band                        |
| 485  | CP ring tilting                     |
| 554–594  | CP ring tilting, deformation        |
| 635  | ring deformation (tetrazine adduct) |
| 800  | C–Cl stretch                        |
| 1010   | CP out of plane CH vibration        |
| 1075   | CP ring stretch                     |
| 1300   | C–O–C = asymmetric stretch          |
| 1385, 1522   | ring stretching (tetrazine adduct)  |

To determine the spatial resolution of the microcontact printing/ink method used in this study, a striped surface pattern (10 µm wide stripe features) on HOPG was generated following the microcontact printing and cleaning procedures described above. Raman spectra (500-700 cm<sup>-1</sup>) with the characteristic Raman active cyclopentadiene ring mode and the tetrazine adduct ring deformation mode were collected by moving the laser spot linearly in 3 µm intervals (Figure 1 d). The sharp increase (from position 3 µm to 6 µm) and decrease (from position 12  $\mu m$  to 15  $\mu m)$  of the adduct intensities indicates that the IEDDA reaction occurs solely on the areas defined by the microcontact printing stamp. It is noteworthy that the well-defined change (>60% over  $3 \mu m$ , Figure S3) in the Raman intensity is indicative of the high fidelity of the transfer IEDDAbased reagents onto the HOPG surface. This suggests that these tetrazine derivatives may be amenable to inkjet printing methods.<sup>[29]</sup>

The unmodified HOPG and Fc-O-Tz modified surfaces were further characterized by XPS. XPS can be used to confirm the presence of elements introduced to the HOPG through the Diels-Alder and retro-Diels-Alder reactions. The survey scan spectra collected at different areas of the modified and nonmodified surface are clearly different. Representative spectra are shown in Figure 2. No other elements are detected in the



high-resolution XPS spectra of the non-modified HOPG. The

Diels-Alder adduct on the HOPG surface (Figure 2b) leads to a

new peak at 400.8 eV and is assigned to N1s. The doublet cen-

**Figure 2.** XPS survey spectrum and high-resolution spectra of Fc-O-Tz-patterned functionalized HOPG. The high-resolution spectra for each element on (modified) and off (not modified) the pattern was collected for comparison purposes. No Fe, N, or Cl were detected on the unmodified regions. The new elements on the modified area are associated with the IEDDA adducts. (a) Survey scan of a clean HOPG surface; (b) survey scan of a modified HOPG surface; (c) Fe2p; (d) C1s; (e) N1s, and (f) Cl 2p1/2 and Cl 2p3/2. The C1s peak originating from the sp<sup>2</sup> carbon of unmodified HOPG arises at 285.0 eV.

Che

3

© 2018 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

These are not the final page numbers! **77** 



tered at about 202 eV is assigned to Cl2p<sub>1/2</sub>/Cl2p<sub>3/2</sub> (202.3 eV/ 200.6 eV). The characteristic peaks of Fe2p<sub>3/2</sub>/Fe2p<sub>1/2</sub> (708.3 eV/ 721.1 eV) were also detected. The ratio of Fe:Cl:N is 1.0:1.0:2.1 (after correction for sensitivity factors), consistent with the elemental ratio (1:1:2) expected for the Diels–Alder adduct. A control experiment was carried out in which the corresponding ferrocenemethanol was applied to an HOPG surface, under the same stamping and purification conditions. The resulting XPS spectra were similar to the pristine HOPG and no new peaks are observed. This is consistent with the tetrazine-derivative compounds being covalently bonded to the HOPG surface rather than that associated by physical adsorption.

Surface modification is an effective way to tune the electronic properties of an HOPG surface.<sup>[6,7]</sup> After the IEDDA reaction of tetrazine with HOPG, its surface conductivity can be evaluated using scanning electrochemical microscopy (SECM).<sup>[16,30]</sup> SECM images were thus obtained with the microelectrode positioned over the modified HOPG surface in a 1.0 mm ferrocenemethanol/0.1 м KCl solution; the microelectrode was poised at  $E_T = 0.35$  V versus Ag/AgCl. The Faradaic current resulting from the oxidization of ferrocenemethanol depends on the electrochemical activity of the substrate.  $^{\scriptscriptstyle [31,32]}$  When the SECM probe approaches an inert surface, a smaller current (negative feedback response), relative to that collected over a conductive surface is observed. The resulting shear-force controlled SECM linear line scan of the patterned HOPG surface (Figure 3 a) reports that the regions of the surface which have been covalently modified exhibit low SECM currents, whereas the pristine HOPG surface remains highly conductive in SECM feedback mode. The variation of the linear scan current with distance is consistent with a modified surface, the feature sizes of which are about 150 µm. The SECM map (Figure 3b) determines that the modified area is a square with dimensions of  $150 \times 150 \ \mu$ m, as per both the feature dimensions of the microcontact master stamp and the optical image thereof. The covalently modified surface exhibits very good stability over the course of the SECM experiment and the SECM images collected after a long immersion time (2 h) of the patterned surface. The delivery of IEDDA reagents to an HOPG surface using microcontact printing methods thus produces a spatially differentiated derivatized surface.



**Figure 3.** SECM characterization of the microcontact printed HOPG surface. (a) line scan; (b) SECM image after 2 h immersion. The working electrode (WE) was biased at  $E_{\rm T}$ =0.35 V vs. Ag/AgCl. An overall scan time of 15 min was required to acquire the SECM map. The line scan and image measurements were acquired at shear-force controlled constant distance mode SECM. The amplitude-controlled shear-force scan parameters were: stimulation amplitude = 120 mV, stimulation frequency = 317 kHz, scan speed = 0.2  $\mu$ m s<sup>-1</sup>, and piezo step size = 3 nm.

# Conclusions

The combination of an IEDDA reaction and microcontact printing yields a relatively simple, highly efficient covalent modification methodology to generate a patterned-modified sp<sup>2</sup> hybridized carbon surface. This modification can be carried out on HOPG surfaces under very mild conditions, for example, room temperature, atmosphere pressure, and catalyst-free. The resulting surface-associated Diels–Alder adducts are characterized by Raman spectroscopy, XPS, and SECM. The IEDDA reaction of tetrazine derivatives with an sp<sup>2</sup> hybrid carbon surface is thus shown to be an effective tool for the covalent modification of 2D carbon nanomaterials and promising for the preparation of carbon-based nano-devices.

#### **Experimental Section**

**Commercial solvents and reagents**: HOPG (SPT-II) was purchased from SPI Supplies (USA) and fresh HOPG surfaces were generated by tape peeling. The compounds guanidine hydrochloride, hydrazine monohydride, 2,4-pentanedione, sodium nitrite, trichloroiso-cyanuric acid, 2,4,6-collidine, and ferrocenemethanol were purchased from Aldrich and used as received. Potassium carbonate (Caledon), chloroform- $d_6$  (Cambridge Isotope Laboratories) were also used as received. Dichlorotetrazine was synthesized following reference 19.<sup>[19]</sup> All solvents were purchased from Aldrich and were used as received.

General instrumentation: <sup>1</sup>H NMR spectra and <sup>13</sup>C NMR spectra were recorded using a Varian Mercury 400 (400 MHz) in deuterated chloroform solution and are reported in parts per million (ppm), with the residual protonated solvent resonance used as a reference. HR-MS (ESI, APCI) analyses were recorded in the McGill University, Department of Chemistry Mass Spectrometer Facility. X-ray photoelectron spectroscopy was collected using a ThermoFisher Scientific K-alpha instrument employing a monochromatic  $AI_{K\alpha}$  Xray source (1486.6 eV) and a hemispherical electrostatic analyzer. Raman scattering data were acquired from dried films using a JY LabRamHR confocal Raman microscope (633 nm laser, 4 mW power). The SECM experiments were carried out using a HEKA scanning electrochemical microscope ELPro scan 1 integrated with shear force unit (HEKA Electronik, Germany). The cell was made from Teflon with a small opening in the middle into which the HOPG sample was tightly fitted. A 25 µm diameter platinum microelectrode (ME) was utilized as the working electrode, a chloridized silver wire as a quasi-reference electrode (Ag/AgCl QRE) and a 0.5 mm diameter platinum wire as a counter electrode (Goodfellow Cambridge Limited, Huntingdon, England). MEs were fabricated inhouse by sealing Pt wires (Delta Scientific Laboratory Products Ltd., Canada) into borosilicate glass capillaries with outer diameter of 1.5 mm, inner diameter of 0.7 mm (Sutter Instrument, USA) and sharpening the probe end to a ratio  $RG = r_{glass}/r_T \approx 10$ , in which  $r_{glass}$ is the radius of the insulating sheath and  $r_{T}$  is the radius of the active ME.

#### Synthesis of Fc-O-Tz

4

Dichloroteterazine (30.0 mg, 0.16 mmol), ferrocene-methanol (29.0 mg, 0.13 mmol), and 17.2  $\mu$ L of anhydrous 2,4,6-collidine (0.13 mmol) were dissolved in 10 mL of anhydrous CH<sub>2</sub>Cl<sub>2</sub> under Ar. The solution turned from orange to dark red in 5 min. The reaction continued for 35 min and the solvent was removed by rotary evap-

Chem. Eur. J. 2018, 24, 1-7 W

www.chemeurj.org

# © 2018 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

# **R** These are not the final page numbers!



oration. Fe-O-Tz was then purified by flash chromatography and gave 42.4 mg of Fc-O-Tz as a dark red crystalline solid (93% yield). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta = 4.75$  (t, J = 4.7 Hz, 2 H), 4.70 (bs, 2 H), 4.27 (t, J=4.7 Hz, 2 H), 4.27 ppm (bs, 5 H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 60 MHz):  $\delta = 175.21$ , 163.66, 80.94, 74.27 (2C), 73.11, 70.26 (5C), 70.05 ppm (2C); HR-MS (APCI), exact mass ( $[M+H]^+$ ,  $C_{13}H_{12}CIFeN_4O$ ) calc. 331.0049; found: 331.0057.

#### The inverse electron demand Diels-Alder reaction between Fc-O-Tz with HOPG

Fc-O-Tz and ferrocenemethnol solutions were prepared by dissolving 1 mg of Fc-O-Tz or ferrocenemethanol in 1 mL anhydrous CH<sub>2</sub>Cl<sub>2</sub>. A fresh HOPG surface was generated by tape peeling immediately before use. 50 µL of the Fc-O-Tz solution was applied to the PDMS stamp surface. The tetrazine ink was allowed to dry for 1 min. The PDMS stamp was applied to the HOPG surface with a force of 10 g cm<sup>-2</sup> for 5 min. The HOPG surface was then rinsed with copious quantities of EtOH and CH2Cl2 to remove the unreacted Fc-O-Tz. The patterned chemical modified HOPG surface was then characterized by Raman spectroscopy, XPS, and SECM.

Control experiments were carried out by applying the ferrocenemethanol solution on HOPG under the same reaction and purification conditions. Raman spectroscopy data and XPS data were collected for comparison.

#### Characterization of the tetrazine derivative modified HOPG surface by Raman spectroscopy and XPS

Raman scattering data was acquired from the HOPG samples using a JY LabRamHR confocal Raman microscope. A HeNe laser light at 633 nm was applied to the sample through a 100× microscope objective, with a nominal power at the source of approximately 17 mW. A neutral density filter was used to reduce the incident laser power at the sample to approximately 4 mW. Spectra were obtained using an 1800 line cm<sup>-1</sup> grating with an integration time of 15 seconds. 10 spectra were obtained. The spectra were collected in the range of 400 to 3100 cm<sup>-1</sup>. Background corrections were performed using Labspec software.

XPS spectra were referenced to the C1s binding energy (B.E.) peak to 285 eV. The 2p<sub>3/2</sub>-2p<sub>1/2</sub> peaks were constrained using a  $2p_{3/2}\!/2p_{1/2}$  peak ratio of 2.0 and a peak separation of 1.6  $\pm$  0.1 eV. Peak-fitting procedures were performed using the software ThermoAvantage (version 4.60) software.

#### SECM imaging study of the patterned Fc-O-Tz modified **HOPG** surface

Electrochemical cleaning of microelectrode (ME) was performed in  $H_2SO_4$  (0.1  $\mbox{m})$  cycling between 1 V and -0.5 V vs. Ag/AgCl until well-defined typical features of platinum were recognized, including H<sub>2</sub> adsorption/desorption, and platinum oxidation/reduction.<sup>[30,31]</sup> SECM line scan and imaging experiments were performed using SECM in shear-force distance control mode to decouple the effect of surface topography from the reactivity on the ME current. In this mode, the Pt ME is scanned at a constant distance above the sample enabling exclusive surface reactivity measurement. The amplitude-controlled shear-force scan parameters used in this experiment were stimulation amplitude = 120 mV, stimulation frequency=317 kHz, scan speed=0.2  $\mu$ m s<sup>-1</sup>, and piezo step size= 3 nm.

#### Acknowledgements

This work was supported by grants from NSERC (R.B.L.) and FQRNT (R.B.L.). The authors thank Dr. Mohamed A. Mezour for his assistance with the XPS analysis.

## **Conflict of interest**

The authors declare no conflict of interest.

Keywords: inverse electron demand · Diels-Alder reaction · microcontact printing · highly ordered pyrolytic graphite · tetrazine

- [1] K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigorieva, A. A. Firsov, Science 2004, 306, 666-669.
- [2] K. S. Novoselov, V. I. Falko, L. Colombo, P. R. Gellert, M. G. Schwab, K. Kim, Nature 2012, 490, 192-200.
- [3] C. Lee, X. Wei, J. W. Kysar, J. Hone, Science 2008, 321, 385-388.
- [4] S. Chen, Q. Wu, C. Mishra, J. Kang, H. Zhang, K. Cho, W. Cai, A. A. Balandin, R. S. Ruoff, Nat. Mater. 2012, 11, 203-207.
- [5] C. K. Chua, M. Pumera, Chem. Soc. Rev. 2013, 42, 3222-3233.
- [6] G. L. C. Paulus, Q. H. Wang, M. S. Strano, Acc. Chem. Res. 2013, 46, 160-170
- [7] J. Li, M. L. Zhou, S. Lang, H. Lu, D. Wang, C. Chen, L. Wan, J. Am. Chem. Soc. 2016, 138, 7448-7451.
- [8] S. Sarkar, E. Bekyarova, S. Niyogi, R. C. Haddon, J. Am. Chem. Soc. 2011, 133, 3324-3327.
- [9] S. Bian, A. M. Scott, Y. Cao, Y. Liang, S. Osuna, K. N. Houk, A. B. Braunschweig, J. Am. Chem. Soc. 2013, 135, 9240-9243.
- [10] L. Daukiya, C. Mattioli, D. Aubel, S. Hajjar-Garreau, F. Vonau, E. Denys, G. Reiter, J. Fransson, E. Perrin, M.-L. Bocquet, C. Bena, A. Gourdon, L. Simon, ACS Nano 2017, 11, 627-634.
- [11] a) B. L. Oliveira, Z. Guo, G. J. L. Bernardes, Chem. Soc. Rev. 2017, 46, 4895-4950; b) A.-C. Knall, C. Slugovc, Chem. Soc. Rev. 2013, 42, 5131-5142.
- [12] M. L. Blackman, M. Royzen, J. M. Fox, J. Am. Chem. Soc. 2008, 130, 13518-13519.
- [13] N. K. Devaraj, R. Weissleder, S. A. Hilderbrand, Bioconjugate Chem. 2008, 19, 2297 - 2299.
- [14] N. K. Devaraj, R. Weissleder, Acc. Chem. Res. 2011, 44, 816-827.
- [15] H. S. G. Beckmann, A. Niederwieser, M. Wiessler, V. Wittmann, Chem. Eur. J. 2012, 18, 6548-6554.
- [16] A. Kumar, G. M. Whitesides, Appl. Phys. Lett. 1993, 63, 2002-2004.
- [17] G. P. Lopez, H. A. Biebuyck, R. Harter, A. Kumar, G. M. Whitesides, J. Am. Chem. Soc. 1993, 115, 10774-10781.
- [18] O. Roling, A. Mardyukov, S. Lamping, B. Vonhören, S. Rinnen, H. F. Arlinghaus, A. Studer, B. J. Ravoo, Org. Biomol. Chem. 2014, 12, 7828-7835
- [19] J. Zhu, J. Hiltz, R. B. Lennox, R. Schirrmacher, Chem. Commun. 2013, 49, 10275-10277.
- [20] J. Zhu, J. Hiltz, M. A. Mezour, V. Bernard-Gauthier, R. B. Lennox, R. Schirrmacher, Chem. Mater. 2014, 26, 5058-5062.
- [21] S. Ni, J. Zhu, M. A. Mezour, R. B. Lennox, New J. Chem. 2017, 41, 12392-12396
- [22] A. J. Bard, F. R. F. Fan, J. Kwak, O. Lev, Anal. Chem. 1989, 61, 132-138.
- [23] A. Nijhuis, J. K. Sinha, G. Wittstock, J. Huskens, B. J. Ravoo, D. N. Reinhoudt, Langmuir 2006, 22, 9770-9775.
- [24] S. Niyogi, E. Bekyarova, M. E. Itkis, J. L. McWilliams, M. A. Hamon, R. C. Haddon, J. Am. Chem. Soc. 2006, 128, 7720-7721.
- [25] R. Zacharia, H. Ulbricht, T. Hertel, Phys. Rev. B 2004, 69, 155406-155407.
- [26] J. O. Sofo, A. S. Chaudhari, G. D. Zarber, Phys. Rev. B 2007, 75, 153401-153404.
- [27] R. Sharma, J. H. Baik, C. J. Perera, M. S. Strano, Nano Lett. 2010, 10, 398-405

Chem. Eur. J. 2018, 24, 1-7 www.chemeurj.org

5

© 2018 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

These are not the final page numbers! 77



- [28] A. Kumar, H. A. Biebuyck, G. M. Whitesides, Langmuir 1994, 10, 1498– 1511.
- [29] M. Singh, H. M. Haverinen, P. Dhagat, G. E. Jabbour, Adv. Mater. 2010, 22, 673-685.
- [30] C. Cannes, F. Kanoufi, A. J. Bard, J. Electroanal. Chem. 2003, 547, 83-91.
- [31] L. Danis, M. E. Snowden, U. M. Tefashe, C. N. Heinemann, J. Mauzeroll, *Electrochim. Acta* 2014, 136, 121–129.
- [32] U. M. Tefashe, M. E. Snowden, P. D. Ducharme, M. Danaie, G. A. Botton, J. Mauzeroll, J. Electroanal. Chem. 2014, 720, 121–127.

Manuscript received: March 16, 2018 Version of record online: **I**, 0000



# **FULL PAPER**

Printing on small scale: An inverse electron demand Diels–Alder reaction combined with the microcontact printing technique introduces, under ambient conditions, a spatially resolved chemical patterning to highly ordered pyrolytic graphite (HOPG) surfaces.



# Printing Chemistry

J. Zhu, J. Hiltz, U. M. Tefashe, J. Mauzeroll, R. B. Lennox\*



Microcontact Printing Patterning of an HOPG Surface by an Inverse Electron Demand Diels-Alder Reaction