Light control over (n, m) - selective aryl bromide like functionalization of substrate supported carbon nanotubes

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Abstract

Diazonium reactions with carbon nanotubes form optical $sp^3$ defects that can be used in optical and electrical circuits. We investigate a direct on-device reaction supported by confined laser irradiation and present a technique where an arbitrary carbon nanotube can be preferentially functionalized within a device by matching the light frequency with its transition energy. An exemplary reaction was carried out between (9,7) nanotube and 4-bromobenzenediazonium tetrafluoroborate. The substrate supported nanotubes of multiple semiconducting chiralities were locally exposed to laser light while monitoring the reaction kinetics in-situ via Raman spectroscopy. The chiral selectivity of the reaction was confirmed by resonant Raman spectroscopy, reporting a 10 meV $E_{22}$ transition energy red-shift only of the targeted species. We further demonstrated this method on a single tube (9,7) electroluminescent device and show a 25 meV red-shifted emission of the ground state $E_{11}$ compared to the emission from the pristine tubes.
INTRODUCTION

Single-walled carbon nanotubes (SWCNTs) are unique one-dimensional crystals with outstanding mechanical, optical, and electrical properties. The properties of the CNTs could be improved by introducing functional groups onto the CNTs surface. Such functionalization can improve intrinsic CNTs properties, merge CNTs properties with those of functional moieties or even create new optical states via defect engineering. The most robust approach is covalent functionalization where a chemical bond is created between functional moieties and the CNT. Recently tremendous attention has been paid to covalent functionalization techniques with aryl-alkane and epoxide groups, because they enable precise control over the defect type and yield novel properties. For fully harvesting such properties in devices, the functionalized CNTs require a reliable integration into electrical and photonic circuits. There are two possible pathways, either the CNT is functionalized before or after integration. An advantage of the first one is that it works with standard solution processed material, unfortunately in that case the lateral position of functional group is not well controlled and might occur not at the center of a cavity or between electrodes but somewhere close to a contact, where optical emission can be suppressed. An alternative approach is to functionalize CNTs directly on a device. For this novel approach a functionalization reactions must be developed for substrate supported configurations.

The reaction between CNTs and diazonium salts (Dz) is expected to be sensitive to visible light. The in-situ functionalization on devices should be controlled by focused laser irradiation, similar to its solution-based counterpart. Aryl ring functionalization first occurs in metallic CNTs, which has been previously used to enrich CNTs by electronic type. In semiconducting CNTs the reaction is inherently slow and takes weeks to succeed, but when light drives the reaction it accelerates to a just few hours. This activation process should be related to the generation of free charge carriers via optical photon absorption, which occurs near transition energies ($E_{11}$, $E_{22}$, etc). The transition energies of the CNT are determined by the (n,m) chirality, therefore offering a pathway for chiral selectivity. Light driven reactions were so far only performed in bulk aqueous, organic solutions, and dried films. The questions remain whether an on-device reaction occurs at a liquid-solid phase boundary, given the limited amount of access points, and whether the reaction at the surface is still light sensitive and chirally
selective. Another challenge is that reaction monitoring by the optical signatures of defect states may be inaccessible in devices. We therefore need to find visible alternatives, such as electrical performance, vibrational spectroscopy, or changes in the energies of the delocalized excitons.

The monitoring of the reaction in-situ is crucial for understanding the reaction kinetics and the physical effects of functionalization such as strain or doping. The evolution of Raman spectra can be used to monitor the reaction in-situ. The covalent bond formation is accompanied by the \( sp^2 \) distortion in the \( sp^3 \) hybridized CNT lattice. This distortion breaks the translational symmetry and introduces a defect state \[20\]. Thus the selection rules for momentum forbidden Raman scattering processes change. The defect induced modes occur \( \sim 1300-1350 \text{ cm}^{-1} \) in most \( sp^2 \) carbons, including graphite\[21\], graphene\[22, 23\], and CNTs\[20\]. The D mode has been widely used in functionalized materials,\[12, 24\] including aryl ring functionalization\[17\]. The increase of the D mode can therefore serve as a scale of the reaction product, since it is proportional to defects concentration. Also additional doping effect, imposed by a functional group, can be detected via Raman\[25\]. The expected changes in the G mode positions of semiconducting CNTs are on the order of 0.5 \text{ cm}^{-1}, [26] and are difficult to analyze ex-situ.

Our manuscript consists out of three sections; in the first we study the reaction kinetics and light sensitivity on a mixed chirality sample. From all chiralities we target (9,7) CNT with 1.58 eV laser and monitor in-situ evolution of the Raman modes. We determine the influence of the photon flux on the reaction rates and products. Further, we investigate functionalization spot and find the defects exclusively in the areas irradiated by light. In the second section we investigate chiral selectivity. The transition energy shifts of three CNT species are investigated by resonance Raman spectroscopy. The red-shift is only found in the targeted (9,7) CNT. With this we establish an additional transition energy-based metric of functionalization. In section three, we apply this metric for a single-tube electroluminescence device\[27\]. The functionalization occurs after CNT integration into a device and its spectral output indicates successful reaction together with a change of electrical transport characteristics.
EXPERIMENTAL METHODS

The very first step is the preparation of the semiconducting CNTs suspension. The nanotubes need to be purified first, in order to remove all metallic species. The HiPco-CNT-suspensions in toluene were prepared using the polymer wrapping technique \cite{28}. The Poly(9,9-di-n-octylfluorenyl-2,7-diyl) (PFO) provided from Sigma Aldrich was used as a polymer surfactant. The excess polymer was removed with the help of size-exclusion chromatography (SEC).\cite{29} The suspensions contain μ-long s-CNTs with almost no m-CNTs and low polymer concentration.

We found that With laser-assisted functionalization (LAF) it is possible to select the desired chirality and use scattered light for monitoring reaction in-situ. The DzBr salt was purchased from Sigma Aldrich. With a molecular weight of 270.82 g/mol and 96 % purity yielding a concentration of 3.5 μmol/g when 1 mg is dissolved in 1 g water. The freshly prepared solution has a pH-value of 3.6. For the laser-assisted functionalization, the DzBr solution was diluted (1:100) to a concentration of 35 nmol/g for exposure to the nanotube.

Experimental setup for in-situ monitoring of functionalization. A Schematic view of the laser-assisted kinetic measurements is given in Figure 1a. The substrate was placed in a plastic container for the LAF step. The drop casted CNTs were covered with 2 ml of deionized water and a glass cover floating on the droplet to overcome the lens effect at the water surface. The measurements were done with excitation powers between 2 and 40 mW with a 5x objective resulting in a power density from 7.9 to 157 W/mm². No spectral changes were observed before Dz compound was added even at the highest laser power.

The light sensitivity was probed by lateral Raman mapping. We mapped the defect density in the entire area around the functionalization spot. After LAF (2mW; 50x objective; 2h), a Raman mapping of the irradiated zone and its surroundings was performed with an Xplora Horiba spectrometer. The same excitation energy as for LAF (785 nm) was used, but an objective with higher magnification (x100, N.A. 0.9) was picked to obtain higher lateral resolution. At each x, y position a Raman spectrum, containing the G and D modes was acquired. These modes were fitted with Lorentzian profiles and the intensity (integrated peak area) of the D mode was divided by the intensity of the G+ mode (LO phonon) in Figure 1b and 2d.

We probed chiral selectivity by comparing targeted and non-targeted species. We analyze
the evolution of transition energies with resonant Raman spectroscopy. The RBMs were recorded before and after LAF (2mW; 50x objective; 2h) functionalization. A tunable excitation system was used with a Ti:Sa laser (Coherent MBR 110) providing excitations from 700 to 1000 nm. The backscattered light was collected by a 50x objective before the functionalization and with an 100x objective after the functionalization to select nanotubes from the reaction centre. A triple grating system of a T64000 Horiba spectrometer equipped with a 900 line per mm grating and a silicon charge-coupled device was used to analyse the backscattered light. Raman shift and intensity were calibrated on a sulphur reference sample. Resonant Raman maps in Figure 4g and h were constructed from calibrated Raman spectral fits.

To demonstrate our technique we fabricated a single tube device and evaluated functionalization induced change in its optical and electrical properties. Devices were prepared from commercial substrates (Active Business Company), which consist of a boron-doped silicon carrier wafer (resistance $\Omega < 0.005 \text{ cm}$) covered with 300 nm of thermal silicon oxide. The wafer was diced to 10x10 mm$^2$ and Pd electrodes with 500 nm gap size were defined by standard electron beam lithography. The toluene-based suspension containing a few-chirality semiconducting nanotubes with diameters 1- 1.2 nm, predominantly (9,7), (8,7), and (8,6) was used. Individual CNTs were deposited from solution onto multiple contact pairs by capacitive coupled ac-dielectrophoresis. The suspension was diluted to a concentration of 1 CNT/µm$^3$ solvent to deposit individual tubes, and a 20 µl droplet was placed onto the device array. A bias between 0.1 and 2 V at frequencies between 100 kHz and 1 MHz was applied between the common drain electrode and the back gate using Agilent 33250 function generator. After 5 minutes the sample was rinsed with toluene to get rid of the excess polymer and annealed for 1.5 hours at 160 °C to improve the contact conductivity. To confirm the deposition of individual CNTs transport characteristics of the devices were measured at ambient conditions in a probe station with TRIAX probes using an Agilent 4155C Semiconductor Parameter Analyzer. For current biasing, we have used for the source and the drain electrode separate source-measurement-units (SMU) and operated the Agilent 4155C in constant current mode. The drain electrode has been set as a reference for the gate voltage which has been applied by a third SMU in constant voltage mode.

For applying our LAF method to our device, the substrate with the devices was covered with the DzBr-solution for 45 minutes and irradiated with 785 nm at 40 mW and 5x mag-
nification. The sample was then rinsed with water, blown dry with nitrogen, and annealed on a hotplate for 5 minutes at 130°C.

Finally, with electroluminescence spectroscopy we studied the influence of the functionalization of the optical properties of the device: Samples were mounted on a custom made sample holder and chip contacts of up to eight devices were bonded onto palladium pads attached to this holder. *In-situ* annealing at 60-70 °C was conducted via the integrated heater at a pressure below 10.6 mbar and the subsequent electroluminescence measurements were carried out without breaking vacuum. The cryostat has a 10 mm diameter optical access via a 0.5 mm thick quartz window and the emitted light was collected with a Zeiss LD-Plan Neofluar objective (40x/0.6) of a customized Zeiss Axiotech Vario microscope and focused with an off-axis parabolic mirror (Thorlabs MPD149-P01, Ag, 25.4 mm, f/4) into an Acton SP-2360 (f/3.9) imaging spectrograph (Princeton Instruments) and dispersed via a 85 G/mm, 1.35 μm blazed grating onto an InGaAs photodiode linear array (PyLoN-IR Princeton Instruments) with 1024 pixels, sensitive from 950-1610 nm. The cryostat is positioned with sub-μm precision by a motorized xy scanning stage (8MTF, Standa) and the working distance between objective and sample surface is adjusted by a high precision objective piezo scanner (P-721 PIFOC / E-665 Piezo Amplifier, Physics Instruments), which allowed precise and stable positioning of the emitter. CNT-devices mounted in the cryostat were driven by an Agilent 4155B Semiconductor Parameter Analyzer. The noise in the spectra in Figure 5b was reduced by using a moving average of 15 periods, after performing all fitting operations.

RESULTS 1. LIGHT SENSITIVITY. KINETICS

At start by investigating the light sensitivity of the reaction and study whether the functionalization can be controlled with light. We drop casted a mixture of several semiconducting CNT chiralities onto the silicon substrate. After the CNTs adhered to the substrate, the sample was covered with water, as shown in Figure 1a. The laser light of 1.58 eV tuned in resonance with the second excitonic transition $E_{22}$ of the (9,7) CNT, was focused onto the nanotubes. The inelastically scattered light was instantly analyzed by a Raman spectrometer. A Raman spectrum after 1 minute illumination is shown is Figure 1b. The highest peak at 1592 cm$^{-1}$ is G$^+$ mode due to the longitudinal vibration (we further omit + symbol). The D mode at 1288 cm$^{-1}$ is proportional to the $sp^3$ defect concentration in the CNT.
FIG. 1. Experimental setup for laser assisted functionalization. (a) Experimental scheme, the nanotubes were drop casted onto the substrate and covered with the aqueous solution. The activation laser of 785nm (1.58 eV) is focused onto the CNTs and backscattered light is analyzed with a Raman spectrometer. After adding the Dz-Br to the solution the functionalization proceeds of the CNT resonant with activation light (highlighted by a red colour). (b) The ratios between the D and G modes with (red) and without (black) addition of Dz-Br with the same illumination density and the ratio between the D and G modes scales with the defect density. We started the laser-assisted functionalization (LAF) by adding 4-bromobenzenediazonium tetrafluoroborate (Dz-Br) to the solution (35 nmol/g). In 2 hours the amount of defect centers produced by covalent functionalization increases yielding a more intense D mode, see inset in Figure 1b. The time evolution of the intensity ratios between the D and G modes is shown in Figure 1c, and clearly reflects all the reaction details. The reference measurement is shown in Figure 1c by black symbols. We used the same experimental conditions without adding Dz-Br. No changes occurred in the Raman spectrum, indicating that in our setup the laser light does not perturb the CNTs in the absence of the reaction agent. While during intense laser illumination one could expect CNTs oxidation or even defects healing, these would only occur at higher laser densities and dry conditions.

Through in-situ functionalization we can follow real-time doping effects. The time evolution of the CNT Raman spectra of the D and G modes during illumination is shown in Figure 1b. The $I_D$ increases with time reflecting the progress in reaction. At the same time, the G mode intensity decreases, Fig. 1b, and shifts to higher energy, Fig. 1c.
FIG. 2. *In-situ* control of the reaction kinetics via laser power. (a) Evolution of the Raman D and G modes during illumination, time increases from the bottom to the top. (b) Integrated intensity and (c) position of the G mode plotted over illumination time. (d) The $I_D/I_G$ over illumination time for 2, 4, 20, and 40 mW laser powers offset each by 0.05 for better visibility. Symbols represent experimental data and line is a kinetic fit by Eq. (1). (e) Reaction rate and (f) reaction yield as function of laser power. Symbols represent experimental data, and lines empirical expressions by Eq. (2).

Intensity decrease is accompanied by a shift (0.5 cm$^{-1}$) and broadening (0.7 cm$^{-1}$) of the G mode due to doping induced by covalent functionalization.\cite{24,33} The doping is a result of additional charge carriers shared by the functional moieties. The displacement of the G mode scales non-linearly with doping,\cite{25,26} and therefore is not an ideal measure of the reaction product. The $I_D/I_G$ ratio, however, does not change with doping,\cite{25} and is better for monitoring kinetics.

The D/G ratio details the number of covalent bonds formed and is directly proportional to the reaction product. Figure\cite{24} shows an increase of covalent bonds under laser illumination for four different laser powers. The $I_D/I_G$ ratio reached 0.1 (0.2) with the lowest (highest) photon density in 120 minutes. We find the reaction kinetics to follow the first-order reaction rate
The law [34]:

\[
\frac{I_D(t)}{I_G} = \frac{I_D}{I_G} \left( 1 - e^{-k_D t} \right) + \frac{I_D}{I_G} \tag{1}
\]

where \( \frac{I_D}{I_G} \) and \( \frac{I_D}{I_G} \) reflect the defects density at infinite and zero reaction time respectively. \( k_D \) is the reaction rate derived from the defect density. The experimental data is fitted by Eq. (1) and the fit is shown in Figure 2 by the solid lines. The parameters are listed in Table I along with the standard fit errors. The defects induced by the reaction can be associated with the reaction yield. The yield \( \frac{I_D}{I_G} \) increases with photon density. Obviously, each successful reaction augments the potential energy barrier required to overcome for the next reaction to occur at the near point. This leads to a saturation of the defect densities after longer illumination times. Denser photon flux promotes further functionalization within the laser spot and leads to higher defect densities. The dependence of reaction yield on laser power (photon flux density) is shown in Figure 2. We suggest that a similar dependence shall be found for a concentration dependence, since the reaction barrier is determined by a laser flux density and the amount of reactant near the CNTs surface. The variation in the energy barrier with photon flux could also be induced by photo gating of the nanotube on the SiO\(_2\)/Si surface,[35, 36] we later perform the chiral analysis to verify these effects. The different energy barriers might be also associated with various binding cites which would pave a new way to control the defects center even better.

### Table I. Laser power control parameters over the diazonium/nanotube reaction rate \( k_D \) ± 10\(^{-3}\) (min\(^{-1}\)) and reaction yield \( \frac{I_D}{I_G} \) ± 5 · 10\(^{-4}\) from Eq. (1), plotted in Figure 2.

| Laser power (mW) | Power density (W/mm\(^{-2}\)) | \( k_D \) (min\(^{-1}\)) | \( \frac{I_D}{I_G} \) \( I_G \) (cm\(^{-1}\)) | D position (cm\(^{-1}\)) | FWHM |
|------------------|-------------------------------|---------------------------|---------------------------------|-------------------|-------|
| 2                | 8                             | 0.024                     | 0.09                            | 1288.8            | 8.6   |
| 4                | 16                            | 0.019                     | 0.14                            | 1289.5            | 8.7   |
| 20               | 79                            | 0.018                     | 0.17                            | 1291.5            | 9.3   |
| 40               | 158                           | 0.018                     | 0.21                            | 1291.7            | 9.4   |

The reaction rate follows an inverse trend compared to the reaction yield. The rate of the reaction decreases with increasing photon density, as shown in Figure 2. This is unexpected since the reaction rate should in principle increase with higher laser power, as
it provides thermal energy to the system, which would lead to enhanced diffusion. A total
reaction rate $k = \frac{k_{D}k_{r}}{k_{D}+k_{r}}$ can be described by an intrinsic rate $k_{r}$ and a diffusive rate $k_{D} \sim T$, where $T$ is the temperature. A non-linear increase of reaction rate with laser power is expected, but the decreasing trend observed. We attribute this counter intuitive behavior to a competing parallel reaction. As commonly known the diazonium cations decompose in water into nitrogen and phenyl when enough thermal energy is given to the system. Higher laser energy induces more local heat development, thus accelerating this reaction.[37] The heat is instantly carried away from the nanotube surface as no heat-induced effects are observed in the Raman spectrum. The competing reaction leads to a retardation of the functionalization due to a reduced concentration of reactant around the nanotube surface. We find that the reaction rate $k$ and the reaction yield $C \left( \frac{I_{D}}{I_{G}} \right)$ from Eq. (1) dependence on laser power follow the empirical expressions:

$$k(P), C(P) = A_{k,C} + B_{k,C} \left( 1 + e^{-k_{p}P} \right),$$

(2)

with $A$, $B$, $k$ as constants ($A_{k} = 7 \cdot 10^{-3}$ min$^{-1}$, $A_{C} = 0.1$ min$^{-1}$, $B_{k} = 0.01$ min$^{-1}$, $B_{C} = 7 \cdot 10^{-2}$ min$^{-1}$, and $k_{p} = 1.5 \cdot 10^{-2}$ mW$^{-1}$). The plots of Eq. (2) with these parameters are shown in Figure 2 by dashed lines. They may be equally applicable for nanotubes on surfaces as well as bulk solutions with low opacity, enabling propagation of the activation light through the entire volume. Two control parameters can be used to achieve the desired functionalization rate, the photon density and the illumination time. When a fast reaction is desired, the highest laser power should be applied. Up to now we investigated the CNTs under the laser spot, we also need to check them in the dark areas.

After the LAF, we rinsed the sample with water multiple times and dried it. The functionalization spot (FS) was examined by spatial Raman mapping of 600 nm resolution. We again assessed the functionalization degree by analysing the D/G ratio which encompasses the number of the new covalent bonds (defects) formed. The D/G ratio is plotted over the lateral position in Figure 3b. The highest degree of functionalization (D/G = 0.4) is observed in the middle of the FS compared to the unperturbed nanotubes outside of the FS (D/G = 0.1). Figure 3a details the characteristic D and G$^+$ Raman modes of semiconducting nanotubes at 1288 and 1592 cm$^{-1}$, respectively, at three different distances from focus centre.[1]

The increase of the defect density within the functionalization spot indicates a successful
FIG. 3. Light sensitivity of the reaction. (a) Raman spectra acquired at different distances from the functionalization spot center. (b) Lateral variation of the intensity ratio between the D and G Raman modes over the functionalization spot excited by 1.58 eV. Horizontal dashed line indicates where the linear profile is taken. (c) The D to G profile as a function of the x position, symbols represent experimental points and line is a fit by Gaussian line shape. The width of Gaussian peak corresponds to the full width at half maximum of the laser spot.

laser assisted reaction. The defect density inside the focus increases from the edges to the middle as shown by the line profile of the D/G ratio in Figure 3c. The defect density follows the Gaussian intensity profile of the laser beam. The full width at half maximum of the profile of 2.2 μm coincides with the width of the laser spot. It suggests that the reaction yield is proportional to the photon flux density (laser power) and functionalization gradients can be generated by laser light. The above experiments were performed at the same excitation energy as activation energy (1.58 eV), thus reporting the effects in (9,7) nanotube. Now we turn to the analysis of other chiralities.
RESULTS II. CHIRAL SELECTIVITY. TRANSITION ENERGIEShiftS (INVESTIGATION VIA RESONANCE RAMAN)

The G and D modes have for all nanotubes similar vibrational energies and are both excited in a broad excitation window of 190 meV, making it impossible to distinguish between chiralities present in the sample. The energies of the radial breathing modes (RBMs) on the other hand depend on tube diameter. We apply resonant Raman spectroscopy to RBMs to access transition energies of each species. Raman spectra in the low energy region at three excitation energies are shown in Figure 4a-c. The modes are index identified as the (8,6) - 247.6 cm\(^{-1}\), (8,7) - 232.5 cm\(^{-1}\), and (9,7) - 219.5 cm\(^{-1}\). We measured the intensity of each mode as a function of laser excitation energies, see in Fig. 4d-f. These Raman profiles are described by third-order perturbation theory:

\[
I_{\text{Raman}}(E_{\text{las}}) = E_{\text{las}}^4 \left[ \frac{M_{\text{exc-ph}}^2 M_{\text{exc-RBM}}}{(E_{\text{las}} - E_{22} - i\gamma)(E_{\text{las}} - \hbar\omega_{\text{RBM}} - E_{22} - i\gamma)} \right]^2,
\]

where \(M_c\) is the matrix element combining exciton-photon and exciton-phonon coupling. \(E_{22}\) is the energy of the second excitonic state and \(\gamma\) is the broadening factor related to the finite lifetime of the exciton. The non-resonant \(E_{\text{las}}^4\) dependence in Eq. (3) is eliminated by calibration on the Raman reference sample. The fits are shown by the solid lines in Figure 4d-f and the parameters are listed in Table I. The transition energies of the pristine and functionalized (9,7) CNT (vertical lines) differ by 10 meV, whereas the transition energy of the (8,6) and (8,7) CNTs remain constant. The difference in transition energies can be also viewed on resonance Raman maps, see Figure 4g,f. The vertical axis represents the laser excitation energy and horizontal Raman shift and the blue (red) colour represents low (high) Raman intensity. The vertical positions of the resonant peaks are different for the DzBr-(9,7) and (9,7), see horizontal lines in Figure 4g,f, whereas the positions of the (8,6) and (8,7) do not change after functionalization. The shift of transition energies occurs due to functional groups that surround the CNT. They form a dielectric layer which alters many body interactions within the tube. A denser dielectric environment leads to a red-shift of the optical transition energies. The shifts of transition energies are broadly used to confirm functionalization. Together with the increase of the D mode (Fig. 2a), the \(E_{22}\) red-shift provides an additional evidence of covalent functionalization.

We suggest the charge carriers photo-excitation to be responsible for chiral selectivity.
mechanism. The laser excites excitons that partly relax into charge carriers. These free charge carriers reduce the reaction barrier, yielding higher reactivity of photo excited CNTs. With this interpretation we conclude that the reaction yield is proportional to the absorption overlay with the laser energy, i.e. an additional activation occurs if $E_{activation}$ is in the range $(E_{22} + \gamma/2, E_{22} - \gamma/2)$. The $\gamma$ is obtained from Raman profiles, see Table II. Additional effect might be provided by the photo carrier generation by the Si/SiO$_2$ interface. This effect appears to be less important, since it equally affects all chiralities, whereas we observe pronounced chiral selectivity in Figure 4d-f. The chiral selectivity of the reaction is demonstrated here between Dz-Br and (9,7) nanotubes, however, we anticipate that this method can be applied to any arbitrary (n,m) chirality and diazonium compound. Finally, we further apply aryl bromide functionalization on individual nanotube pre-integrated into a device.

**TABLE II.** Second transition energy $E_{22}$ for pristine nanotubes (prist) and DzBr-CNT (func) acquired by fitting the resonance Raman profiles in Figure 4b-c, detuning is $E_{22}-E_f$ ($E_f = 1.58$ eV) and $E_{22}$ shift = $E_{22}^{func} - E_{22}^{prist}$. The average $E_{22}$ ($\gamma$) error is $\pm 1.5$ (3.5) meV.

| (n,m) RBM position detuning $(cm^{-1})$ | $E_{22}^{prist}$ (meV) | $E_{22}^{func}$ (eV) | $E_{22}$ shift (meV) | $\gamma_{prist}$ (meV) | $\gamma_{func}$ (meV) |
|----------------------------------------|------------------------|---------------------|---------------------|------------------------|------------------------|
| (8,6) 248                             | 84                     | 1.65                | 1.65                | -0.7                   | 32                     | 37                     |
| (8,7) 233                             | 136                    | 1.71                | 1.71                | 0.8                    | 31                     | 39                     |
| (9,7) 220                             | -22                    | 1.55                | 1.54                | -10.5                  | 32                     | 28                     |

**RESULTS III. DEVICE INTEGRATION, ELECTROLUMINESCENCE**

Now we discuss the application of the LAF method to a CNT device. A sketch of the device is shown in Figure 5a, where a nanotube is positioned between two electrodes by dielectrophoresis, see methods section. An equal amount of holes and electrons is injected through opposite electrodes, followed by recombination in the middle and emerging photoluminescence.[27, 44] A spectrum of emitted light from such a device prior functionalization is shown in Figure 5b (green trace). The peaks around 0.9 eV and 0.8 eV are associated with emission from exciton (electron-hole pair) [45] and trion (charged exciton)
FIG. 4. Chiral selectivity of the reaction. Radial breathing modes before (green) and after (red) functionalization excited at three different wavelengths (a) 1.57 eV, (b) 1.66 eV, and (c) 1.72 eV. Intensities of the RBMs as function of excitation energy (d), (e), (f) for (9,7), (8,7), and (8,6) nanotubes, respectively. The symbols represent the experimental data before (green) and after (red) functionalization. Symbols represent experimental data and lines are the fits with Eq. (3). Vertical colored lines mark the $E_{22}$ transition energies. The vertical purple line indicates the laser energy $E_f$, used to drive the functionalization. Resonant Raman maps of (g) pristine and (h) DzBr-CNTs with indicated chiralities and transition energies marked by horizontal lines of the (9,7) $E_{11}$ state, as discussed by Gaulke et al.[27] The absence of other peaks indicates that this device most likely comprises only a single nanotube. The position of the $E_{11}$ emission varies by up to 3 meV when driven at different DC currents.

The LAF was then performed on the device, and to ensure that aryl ring binds the nanotube in the middle we applied a PMMA mask with a 50nm slit centred between the electrodes. The emission of the 4-Bromophenyl functionalized device was collected for a series of currents as shown in Figure 5b by red colour. The emission of the ground $E_{11}$ excitonic state is found at 0.92 eV, which is red-shifted by approximately 20 meV compared to the emission of the pristine device. The shift of transition energy indicates successful
FIG. 5. Aryl bromide functionalization of an electroluminescent (9,7) nanotube device. (a) Device sketch and geometry. (b) Electroluminescence spectra of (9,7) nanotubes at different currents before (green) after functionalization (red). Peaks were fitted by a single Lorentzian (see filled peaks). (c) Transconductance curves measured before and after functionalization.

Aryl bromide functionalization changes the doping level of the nanotubes. This manifests in a suppression of the (9,7) trion (charged exciton) at 0.8 eV emission. However this effect is stronger than expected, additionally, the \( E_{11} \) trion might be suppressed by the defect formation, as reported for two-dimensional excitons.\[16\] Further, the Fermi level shift can be seen in the transconductance curves, shown in Figure 5c. The p-type conductance is typical for CNTs in contact with Pd electrodes mounted onto SiO\(_2\)/Si surfaces due to the Schottky barrier for holes being smaller than for electrons. The positive threshold voltage for current switching indicates initial p-doping of the device which reduces to lower gate voltages after functionalization. The functionalization induced doping effect agrees well with Raman spectroscopy data, where a broadening and shift of the G mode was observed. Thus,
the functionalization of semiconducting CNTs is detectable in electrical transport data, as have been previously reported for metallic nanotubes. \cite{47, 48}

The origin of the red-shift both of the second excitonic state (obtained via Raman excitation mapping) and the first excitonic state (obtained by EL spectroscopy) could be induced by the dielectric screening of the excitons. \cite{42} The screening might be provided by the aryl rings covering the nanotube surface. An alternative physical effect providing the shift of excitonic levels can be strain, \cite{24, 33} however, strain along the nanotube axis causes shifts of the second ($E_{22}$) and first states ($E_{11}$) in opposite directions, \cite{49} which is not the case in our system. Therefore dielectric screening appears to be the dominant mechanism influencing optical properties of functionalized CNTs. Note that the lateral control of the reaction centre was improved past the diffraction limit \cite{19} by applying polymer masks and electron beam lithography. Furthermore, the on device functionalization scheme can be of use for other $sp^2$ hybridized nanocarbons with optical transitions in the visible wavelength range such as twisted graphene layers, graphene nanoribbons, and graphene quantum dots. \cite{16, 50, 51}

**CONCLUSIONS**

A novel method that enables a local and chirality-selective covalent functionalization of nanotubes on surfaces and in devices was successfully demonstrated. Laser assisted functionalization of (9,7) nanotube with 4-bromophenyl was studied by spatial Raman mapping of defect density, which confirmed the light sensitivity of the reaction. The nanotubes inside the illumination spot were functionalized, whereas the non-illuminated areas remained unperturbed. The influence of the photon flux density on reaction kinetics was explored by *in-situ* reaction monitoring. The reaction product increased and reaction rate decreased with laser power. The drop of reaction rate with the increase of photon flux reveals a competing mechanism, and could be due to Diazonium salt decomposition activated by local heat. We proposed empirical expressions for controlling the reaction kinetics applicable both to the processes on the surface and in solutions with low opacity.

To test chiral selectivity of the reaction, we compared $E_{22}$ transition energies of the pristine and functionalized nanotubes before and after functionalization. The transition energies were determined by resonant Raman spectroscopy. The $E_{22}$ of (9,7) nanotube red shifted by 10 meV in contrast with $E_{22}$ of the (8,6) and (8,7) retaining their positions. These
two chiralities were out of resonance with the laser energy during functionalization. Chiral selectivity was achieved by matching the laser light energy with the optical transition of the (9,7) nanotube only.

We applied the laser-assisted aryl bromide functionalization to an electroluminescent device made of (9,7) nanotube. The reaction centre was controlled beyond the diffraction limit by a 50 nm opened PMMA slit mark. The functionalization yielded a 25 meV red-shift of the ground optical state ($E_{11}$) electroluminescence. A red shift of the first (EL) and the second (resonance Raman) transitions evidences dielectric screening of the exciton wave function by molecules. The transport characteristics of the functionalized device and Raman analysis suggest a doping effect provided by the functional group. We therefore conclude that laser-assisted on device covalent functionalization opens a route towards nanoscale engineering of trapped excitonic states for optoelectronic circuits.

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