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Chapter 6

Ultra-sensitive ethene detection on graphene field effect transistors using copper(I) scorpionate complexes.

The detection of ethene at biologically relevant concentrations – as low as parts per billion by volume (ppb) – requires extraordinary sensitivity of the sensor. In this Chapter we describe a graphene field-effect transistor (GFET) functionalized with air-stable copper(I) hydridotrispyrazolylborate complexes capable of rapid and sensitive detection of ethene gas. The GFET exploits the remarkable physical and chemical properties of graphene and tailored copper(I) compounds demonstrating the capability of reversibly binding ethene gas at the required ppb concentrations. A spectrochemical series of fluorinated hydridotrispyrazolylborate ligands was used to systematically study the influence of the electronic properties of the copper(I) complexes on the response and sensitivity of the GFET. The use of these tuneable ligands provided systematic influence over the electron densities of the resulting complexes while keeping the steric environment of the copper(I) ions constant. The resulting GFETs offer ethene detection below 100 ppb and offer the possibility of the development of small devices for rapid, sensitive ethene detection for agricultural and food transportation applications.

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6.1. Introduction

Ethene is a gaseous analyte that is particularly important in agri- and horticulture where it serves as a hormone for climacteric plants.\textsuperscript{1-3} Ethene gas is a highly diffusive, relatively unreactive gas that induces ageing responses in plants in concentrations as low as parts per billion (ppb) by volume. Recently, the use of sensitized single-walled carbon nanotubes (SWCNTs) as a sensor for ethene has been reported with which sensitivity of 500 ppb was reached.\textsuperscript{4} The sensitizer consisted of a hydridotrispyrazolylborate copper(I) complex which is known for its ability to coordinate strongly to ethene molecules.\textsuperscript{5} Unfortunately, the desirable properties of SWCNTs such as their excellent surface-to-volume ratios are offset by their undesirable properties. The preparation of bulk samples of SWCNTs is typically associated with difficulties such as their low dispersibility in various solvents and generally plagued by poor reproducibility as a result of impurities, defects and unpredictable and unstable junctions between the SWCNTs. As a consequence FET-type electronic behaviour is typically only clearly observed in single nanotubes or arrays of carefully oriented SWCNTs and not in randomly placed bulk samples.\textsuperscript{6-9} Furthermore it remains unclear if the sensing responses of SWCNTs are the result of modulation of the junctions and defects, the surfaces of the tubes or a combination of the two. The use of graphene instead of SWCNTs allows for the exploitation of the all-surface-atom makeup offered by carbon allotropes like graphene and SWCNTs without the aforementioned practical problems.

A particularly promising example of graphene-based electronics is the class of graphene-based field effect transistors (GFETs). In GFETs the electrical conductivity of graphene is modulated using external electrical fields (i.e. the field effect to which this type of transistor owes its name).\textsuperscript{10} The application of external electrical fields is typically done using back-gating, but can also be done by binding charged molecules close to the graphene surface.\textsuperscript{11} The two-dimensional nature of graphene and the concomitant extremely high surface to volume ratio mean that GFETs are excellently suited for chemical sensing. GFETs have been used to detect individual molecules of NO\textsubscript{2}, showing the extreme potential offered by graphene’s unusually high sensitivity to external electrical fields.\textsuperscript{12} Less reactive gases such as ammonia, water vapour and carbon monoxide can also be detected using graphene, typically with sensitivities at the ppm level or lower.\textsuperscript{13} The mechanism of detection of these gases lies in the ability of the detected molecules to oxidize or reduce the
graphene, thus doping the material with holes or electrons, which results in a change in the conductivity of graphene.

It has been shown that impurities on the graphene, such as residual materials from the fabrication and deposition steps, are likely to be responsible for the reactivity with many of the analyte gases.\(^{[14]}\) Thoroughly cleaned samples of graphene show little to no response to analytes that before cleaning induced strong electrical responses. This finding indicates not only that the, potentially undesired, chemical reactivity towards contaminant gases such as NO, CO and NH\(_3\) can be eliminated by thorough cleaning of the graphene, but also that apparently the graphene can be sensitized greatly to particular analytes by the introduction of ‘tailored impurities’. Using this principle, custom-made sensitizers can be designed to modify the graphene layer for the detection of otherwise difficult to detect, relatively unreactive molecules. The use of tailored sensitizing layers for specific target compounds has been explored previously in liquid gated GFETs sensitized using labels for charged biomolecules.\(^{[15]}\) For gas sensors the use of sensitized graphene is typically limited to the use of transition metal oxide nanoparticles.\(^{[16]}\) Examples of molecule-sensitized graphene gas sensors are very rare and typically include the use of macromolecules like DNA, polyaniline or poly(methylmethacrylate).\(^{[17-19]}\)

The physical and electrical properties of graphene coupled with the possibility for significant sensitization offers promise for the detection of ethene gas with the required sensitivity and reproducibility. The copper(I) complexes shown in Scheme 6.1 were selected for their ability to reversibly bind ethene gas in air.

![Scheme 6.1](image)

**Scheme 6.1.** [Cu(Tp\(^{CF_3_4-R=Me}\))(MeCN)] (left, R = NMe\(_2\), OMe, H, F, Cl or CF\(_3\)) and [Cu(Tp\(^{CF_3_3}\))(MeCN)] (right). The third pyrazole ring is equivalent to the two that are depicted and is indicated as “-[]=“ for clarity.

The trifluoromethyl groups in the 3-positions of the pyrazole rings on the hydridotrispyrazoly!borate ligands serve to oxidatively stabilize the copper(I)
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center while the 4-substituted phenyl rings on the 5-positions of the pyrazoles offer good interaction with the graphene through π-stacking. Additionally the phenyl rings can be modified through substitution to alter the electron density at the copper(I) center while leaving the steric environment around the copper(I) center unaffected. The acetonitrile ligand is labile and can easily be displaced by ethene during the operation of the sensor.

The copper(I) complexes of the hydridotrispyrazolylborate ligands shown in Scheme 6.1 are capable of binding ethene and carbon monoxide and the resulting compounds have electronic properties that can be related to the Hammett parameter of the substituent on the phenyl ring. Combined with the unrivalled sensitivity of graphene to changes in the local environment these copper compounds thus offer an opportunity to systematically study the chemistry and kinetics of an ethene-sensitive GFET. The complex [Cu(TpCF3)2(MeCN)] was included in this work as it has been used previously as the sensitizer in a chemiresistive ethene sensor based on SWCNTs. This compound has a binding “pocket” at the copper(I) ion that is highly similar to those in the other copper(I) complexes used in this work.

Even though the use of acetonitrile adducts in GFET devices intended for the detection of ethene may not seem immediately obvious a number of compelling reasons justify their use. Firstly, the thin layers of complex molecules applied to the GFET are expected to be able to completely exchange their ancillary ligands. Once dissociated from the copper(I) centers the acetonitrile molecules will enter the vapor phase and rapidly diffuse away from the sensor surface. The resulting concentrations of acetonitrile will be so low as to effectively prevent reassociation with the complex molecules on the surface. Particularly in a stream of gas the effective concentration of acetonitrile will be effectively zero. Secondly, the acetonitrile complexes offer facile access to air-stable, soluble complexes with coordination geometries that are highly similar to those of the corresponding ethene complexes. In principle the ethene or carbonyl complexes would have been similarly applicable except for their generally lower solubilities in dichloromethane which may interfere with techniques such as dip-coating. Finally the acetonitrile complexes represent a relatively rare class of copper(I) hydridotrispyrazolylborate compounds thus offering a chance to study their properties using the systematically varied substituents of the spectrochemical series shown in Scheme 6.1.
6.2. Results and Discussion

6.2.1. Synthesis and analysis of the copper(I) complexes

The acetonitrile complexes were prepared in a metathesis reaction between the sodium salts of the hydridotrispyrazolylborate ligands and [Cu(MeCN)]SbF₆ in DCM and were typically obtained in high yields. After stirring overnight the suspended NaSbF₆ byproduct was removed by filtration after which the complexes could be obtained by evaporation of the solvent. The notable exception was [Cu(Tp^{CF3,4-PPh})(MeCN)] which was found to be particularly insoluble in DCM and had to be extracted into toluene before filtration. The complexes were further purified by recrystallization from DCM (or toluene in the case of [Cu(Tp^{CF3,4-PPh})(MeCN)]) using pentane as a counter solvent. All complexes were obtained as white microcrystalline solids that showed no degradation upon exposure to light and air for periods of months.

The acetonitrile complexes were analysed using ¹H, ¹³C and ¹⁹F NMR and showed the expected resonances based on the structurally almost identical carbonyl and ethene complexes. Resonances attributed to the methyl groups of the acetonitrile ligands were observed around 2.3 ppm on ¹H NMR and around 2.7 ppm on ¹³C NMR. The trends with respect to the substituent observed in the resonances of the ethene and carbonyl ligands are not apparent in the acetonitrile complexes. Most likely the nitrile groups effectively shield the acetonitrile protons from the electronic effects of the hydridotrispyrazolylborate ligands. Additionally the orientations of the protons away from any other atoms in the molecule precludes through-space interactions which further eliminates the electronic effects of the hydridotrispyrazolylborate ligands. The trifluoromethyl groups are located around ~60 ppm on ¹⁹F NMR which is typical for aromatic trifluoromethyl groups. Highly similar chemical shifts were reported for the structurally comparable complexes [Cu(Tp^{CF3})(C₆H₄)], [Cu(Tp^{CF3,Ph})(C₆H₄)] and [Cu(Tp^{CF3})(C₆H₄)]. No trend was found in their exact resonances with respect to the electronic properties of the copper(I) centers due the low polarizability of trifluoromethyl groups and the orientations of the fluoride atoms away from the other atoms in the complex molecules. The ¹⁹F signal for the fluoro substituent on the phenyl ring was observed as a triplet of triplets at ~113.25 ppm which indicates a somewhat electron-poor phenyl ring.

To confirm the premise that the acetonitrile complexes are structurally highly similar to the carbonyl complexes of these hydridotrispyrazolylborate ligands
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the structure of one such acetonitrile complex determined. [Cu(Tp\textsuperscript{CF3,4-OMePh})(MeCN)] crystallized from DCM as large transparent blocks suitable for single crystal X-ray crystallography. The structure of [Cu(Tp\textsuperscript{CF3,4-OMePh})(MeCN)] (shown in Figure 6.1) was found to consist of a tetrahedrally coordinated copper(I) center with three nitrogen-donors from the hydridotrispyrazolylborate ligand and one nitrogen donor from the acetonitrile ligand. The hydridotrispyrazolylborate ligand is coordinated in the expected facial arrangement with Cu–N\textsubscript{Tp} distances of 2.0745(14), 2.0772(14) and 2.1096(14) Å, the Cu–N\textsubscript{MeCN} distance is 1.8813(14) Å. The observed distances are slightly longer than those observed in [Cu(Tp\textsuperscript{CF3,4-OMePh})(CO)] which has Cu–N\textsubscript{Tp} distances of 2.038(2), 2.062(2) and 2.075(2) Å and a Cu–CO distance of 1.793(3) Å. In [Cu(Tp\textsuperscript{CF3,4-OMePh})(C\textsubscript{2}H\textsubscript{4})], the Cu–N\textsubscript{Tp} distances are 2.026(4), 2.046(4) and 2.224(4) Å (see Chapter 5).

The complex has approximate three-fold rotational symmetry that is broken by varying degrees of rotation of the phenyl rings with respect to the pyrazole rings; the dihedral angles between the phenyl and the pyrazole rings are 46.0(2)°, 55.7(2)° and 60.6(2)°. The differences in the observed distances in the ethene, carbonyl and acetonitrile complexes are likely attributable at least in
part to crystal packing effects. Similarly, the different dihedral angles between the phenyl rings and the pyrazoles are most likely caused by \( \pi \)-stacking in the crystal lattice as the rings have some rotational freedom.

6.2.2. Structural characterization of the GFET devices

The GFET devices (see Figure 6.2) were prepared by wet-transfer of graphene onto highly p-doped silicon substrates with 288 nm silicon dioxide insulator layers. Using atomic layer deposition (ALD) gold electrodes were applied directly on top of the graphene to ensure good contact with the smallest possible contact resistance and the best possible mechanical stability.

![Diagram of GFET devices](image)

**Figure 6.2.** Schematic view of the GFET devices. A highly p-doped silicon wafer with a 288 nm thick SiO\(_2\) insulating layer bears a strip of graphene with source and drain electrodes patterned on top (spacing ~1 mm). The graphene is functionalized with a thin layer of copper(I) hydridotrispyrazolylborate complex. The drain electrode and backgate are grounded, \( V_G \) = backgate potential vs the source electrode, \( V_{sd} \approx 1 \) mV.

Mechanical stability is important as vibrations between non-intimate contacts, such as spring-loaded pins, can result in additional electrical noise during operation of the GFET devices.
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In order to fully exploit the potential for sensitive ethene detection offered by graphene-based devices it is important to assemble the devices as reproducibly as possible. The operation of a GFET is highly dependent on the formation of thin, homogeneous layers of the complexes on the graphene surface. The layers should ideally be of homogeneous thickness so as not to form local “puddles” of charge which can cause scattering of charge carriers in the graphene as scattering is a source of noise. Likewise thin layers are required as the field effect is strongest close to the graphene surface and thick layers would hamper permeation of the analyte gas to the lower layers. To achieve the desired full-surface coverage of the graphene with thin layers of the copper complexes the well-known ability of carbon materials to adsorb dissolved molecules was exploited. The copper(I) trispyrazolylborate acetonitrile complexes were applied to the graphene surface by immersion of the complete devices in solutions of the copper complexes in DCM after which the samples were thoroughly rinsed to remove excess material. To evaluate the resulting layers for thickness and homogeneity samples thus prepared were analysed using ellipsometry and AFM.

Figure 6.3. Space-filling representation of the crystal structure of [Cu(Tp\textsuperscript{CF3,4,OMePh})(MeCN)] as assumed to adsorb to a graphene surface.

Using ellipsometry the thickness of the layers was studied and was found to range from 2.0(1) nm in the case of [Cu(Tp\textsuperscript{CF3,4F-Ph})(MeCN)] to 3.7(1) nm for [Cu(Tp\textsuperscript{CF3,4CF3-Ph})(MeCN)] (see Figure 6.4). The use of [Cu(Tp\textsuperscript{CF3,4F-Ph})(MeCN)] was found to result in the thinnest layers but may be less suitable for comparison with the other samples as the solubility of [Cu(Tp\textsuperscript{CF3,4F-Ph})(MeCN)] in dichloromethane is too low to reach the desired concentration of 10 mM used for dip-coating of the other compounds. If [Cu(Tp\textsuperscript{CF3,4F-Ph})(MeCN)] is excluded
from the series the thinnest layer observed was found for \([\text{Cu(Tp}^{\text{CF3}3\text{Ph}})(\text{MeCN})]\) at 2.46(9) nm. The layer thicknesses do not appear to correlate to the polarity of the complexes, rather it appears that properties such as the steric bulk of the complexes and differences in their packing on the graphene surface are responsible. As is described in Chapter 4 the layer thicknesses corresponding to multiple times the height of a monolayer assuming the complexes adsorb side-on. For example, using the crystal structure of \([\text{Cu(Tp}^{\text{CF3}3\text{4-OMePh}})(\text{MeCN})]\) the thickness of a monolayer was estimated to be approximately 0.8 nm (see Figure 6.3), the layer on graphene of this compound was determined to be 3.31(8) nm thick amounting to approximately 4 monolayers.

![Figure 6.4](image)

**Figure 6.4.** Layer thicknesses obtained by ellipsometry of the multilayers of the complexes \([\text{Cu(Tp}^{\text{CF3}3\text{4-RPh}})(\text{MeCN})]\) labeled with their R-groups vs. the Hammett \(\sigma_p\) parameters of the substituents. Error bars indicate standard errors.

For the complex \([\text{Cu(Tp}^{\text{CF3}3\text{2}})(\text{MeCN})]\) a layer thickness of 1.68(9) nm was obtained. Surprisingly the residence time in the solution has little effect on the layer thickness of \([\text{Cu(Tp}^{\text{CF3}3\text{2}})(\text{MeCN})]\), incubation times of 1, 10 or 100 minutes resulted in layer thicknesses of 1.44(7), 1.68(9) and 1.371(21) nm respectively. The observed variation in thickness indicates that, even though individual samples show very homogeneous layer thicknesses some variation is still possible. Most likely the exact amount of material that is washed away during rinsing varies somewhat per sample depending on factors such as the
amount and temperature of the solvent and the surface roughness of the graphene onto which the molecules are adsorbed. As the widest diameter of \([\text{Cu}(\text{TPC})_2](\text{MeCN})\) is essentially the same as of \([\text{Cu}(\text{TPC})_4](\text{MeCN})\) the observed layer thicknesses of approximately 1.5 nm must correspond to a layer composed of one or two monolayers.

In order to better understand the packing of the copper(I) complexes on the graphene surface the samples were studied using atomic force microscopy (AFM). The dip-coated samples showed no clear signs of self-assembly on the graphene surface, instead disordered surfaces were observed. The surfaces of \([\text{Cu}(\text{TPC})_4](\text{MeCN})\), \([\text{Cu}(\text{TPC})_4](\text{MeCN})\) and \([\text{Cu}(\text{TPC})_4](\text{MeCN})\) looked similarly rough but the scale of the observed features varied. Graphene coated with \([\text{Cu}(\text{TPC})_4](\text{MeCN})\) (see Figure 6.5) showed a relatively homogeneous surface with features that lack obvious geometry ranging from tens to hundreds of nanometers in size. The step height of the darker (lower lying) and lighter (higher) features was found to be approximately 0.7–0.8 nm which suggests \([\text{Cu}(\text{TPC})_4](\text{MeCN})\) to form a pitted surface composed of disordered monolayers.

![AFM image](image)

**Figure 6.5.** AFM image of the surface of \([\text{Cu}(\text{TPC})_4](\text{MeCN})\) on graphene. The height traces on the right show the valley (blue) and the ridge (red) indicated in the image.

\([\text{Cu}(\text{TPC})_4](\text{FFPh})\) (Figure 6.6) and \([\text{Cu}(\text{TPC})_4](\text{CF3Ph})\) (Figure 6.7) on graphene form structures that are comparable to those formed by \([\text{Cu}(\text{TPC})_4](\text{MeCN})\). \([\text{Cu}(\text{TPC})_4](\text{FFPh})\) appeared to form a more finely grained surface and \([\text{Cu}(\text{TPC})_4](\text{CF3Ph})\) formed a rough surface with ridge features of intermediate size.
The surface of $[\text{Cu(Tp}^\text{CF}_3,4,4\text{-CF}_3\text{Ph})\text{(MeCN)}]$ showed small multilayer domains before exposure to ethene. Upon exposure to ethene the surfaces of both $[\text{Cu(Tp}^\text{CF}_3,4,4\text{-Ph})\text{(MeCN)}]$ and $[\text{Cu(Tp}^\text{CF}_3,4,4\text{-CF}_3\text{Ph})\text{(MeCN)}]$ assumed more diffuse textures which were clearly distinct from their former states.

To investigate if the layers are disordered from the first monolayer or if disorder sets in only when the layers build up, monolayer samples were prepared by drop casting dilute (approximately 1 µM) solutions of $[\text{Cu(Tp}^\text{CF}_3\text{)}\text{(MeCN)}]$ and $[\text{Cu(Tp}^\text{CF}_3,4,4\text{-CF}_3\text{Ph})\text{(MeCN)}]$ in DCM on freshly cleaved HOPG (highly oriented pyrolytic graphite). The concentration of the drop-casting solution was chosen such that the resulting surface coverage on HOPG would not exceed a monolayer. HOPG was chosen over CVD graphene as freshly cleaved HOPG offers convenient access to large, flat, contiguous surfaces of high quality graphene.
[Cu(Tp(CF₃)₂)(MeCN)] was found to assemble on HOPG into monolayer domains with the expected thickness of approximately 0.8 nm and areas of tens to hundreds of nanometers (see Figure 6.8). Lying between these larger domains are numerous smaller, strand-like structures of the same height.

**Figure 6.8.** AFM images of [Cu(Tp(CF₃)₂)(MeCN)] on HOPG. The complex forms large domains of monolayers (left). On the right the same area is shown after exposure to ethene gas. The features on the surface show signs of diffusion.

The domains have no obvious shape or structure indicating a limited degree of interaction between the adsorbed complex molecules. The sample was then exposed to pure ethene gas during a scan of the atomic force microscope. The result was dramatic; the surface structures showed clear signs of diffusion with the strand-like structures disappearing altogether and the larger structures changing size and shape. The surface of the sample resolved to show layers with a step height of approximately 0.8 nm. These observations can be explained by the formation of a mixture of [Cu(Tp(CF₃)₂)(MeCN)] and [Cu(Tp(CF₃)₂)(C₂H₄)] on the surface of the sample. Evidently the compounds are not structurally similar enough to co-crystallize (or co-assemble) on the HOPG surface resulting in diffusion of the previously much more ordered surface.

The formation of layers and structures of various adsorbates on flat surfaces as observed with AFM and ellipsometry depends on a numbers of factors, particularly surface-adsorbate stacking interactions, adsorbate-adsorbate stacking interactions and lattice mismatch between the surface and the crystalline phase of the adsorbate. If stacking interactions between the surface and the adsorbate dominate layer formation will proceed via the initial formation of a monolayer followed by the subsequent formation of layers on top of the monolayer (a form of epitaxial growth known as Frank-van-der-Merwe growth). In contrast, if interactions between the adsorbate molecules
dominate layer formation will not occur and crystalline structures will form instead (known as Volmer-Weber growth). Typically neither of the stacking interactions dominates by a large degree and a stepwise transition from Frank-van-der-Merwe growth to Volmer-Weber growth occurs instead (known as Stranski-Krastanov growth). As the layers grow the lattice mismatch between the substrate and the adsorbate causes the dominant mode of adsorption to switch from layer-by-layer growth to crystalline growth.

The rough, multi-layered surfaces observed in the AFM images of the dip-coated samples indicate that there is indeed a transition from the ordered monolayer growth to a less regular form of surface coverage. The absence of obvious two-dimensional organisation in the monolayers of [Cu(Tp\textsuperscript{CF3}2)(MeCN)] indicates a lack of interactions between complex molecules. In contrast, such interactions do appear to be present in [Cu(Tp\textsuperscript{CF3,4-CF3Ph})(MeCN)], which formed multi-layered structures despite being formed from a solution that was too dilute to cover the entire surface in a multilayer. Evidently the incorporation of a phenyl ring in the ligand adds a sufficient amount of \(\pi\)-stacking interactions between the complex molecules to allow for the formation of multilayers with large domains. The comparatively thin multilayers of [Cu(Tp\textsuperscript{CF3}2)(MeCN)] likely result from a lack of such stacking interactions. Possibly more layers form during the dip-coating procedure which are washed away during the rinsing step afterwards. The degree of stacking interactions between the complex molecules would then be at least partially responsible for the resulting thickness of layers that remain after the rinsing step. As the ellipsometry measurement showed the effect not solely to be the result of the polarity of the complexes, likely the steric bulk of the different substituents overshadows the polarity as the dominant factor.

The ability of molecules to diffuse on the surface of HOPG (and thus graphene) has important implications for the understanding of GFET devices sensitized with copper(I) hydridotrispyrazolylborate compounds. If the copper complexes can diffuse across the graphene surface the operation of the sensor is not reliant on mechanisms involving single complex molecules. Instead the formation of self-assembled structures or multinuclear species (or combinations of the two) can be considered as possible states or intermediates in the functioning of the devices.
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6.2.3. Electronic characterization of the GFET devices

The physical structure of the applied layers of copper complex has a direct influence on the electronic properties of a GFET device. Changes in the charge carrier density in the graphene result from changes in the electric field through the graphene (the field effect) which can be detected as a change in the conductance of the graphene.

In order to determine a convenient layout for the GFET devices the performance was compared between devices with small (several μm²) and larger (several mm²) graphene surface areas. A determining factor for the performance of a sensor is its signal-to-noise ratio; larger devices will give rise to larger signal-to-noise ratios. Large devices are also simpler to fabricate, a considerable benefit when many devices are required. A downside of using larger surfaces of graphene is the larger shift of the Dirac point (ΔV_D) away from V_G = 0. This shift is the result of trapped charges on the substrate and defects such as pinholes in the SiO₂ layer. Trapped charges (including trapped ions such as ammonium, sodium and potassium) have an electrical field that influences the charge-carrier density of the graphene which effectively dopes the graphene. Pinholes in the SiO₂ layer are the result of fabrication errors and cause uneven coupling and leak currents between the backgate and the graphene which influences ΔV_D. Additionally, as the area of the graphene increases the variability in its characteristics (such as conductivity and ΔV_D) will increase due to the larger number of defects such as holes, tears, grain boundaries and ripples in the graphene layer. In order to remove the influence of the graphene on the outcome of the experiments the transconductance (g_m) of the GFET devices was used to normalize the responses (see Equation 6.1 and Equation 6.2).

\[
g_m = \frac{\partial I_{sd}}{\partial V_G} \big|_{V_G}
\]

Equation 6.1. Definition of the device transconductance \(g_m\). \(g_m\) is defined as the partial derivative of the \(I_{sd}/V_G\) curve at a given potential \(V_G\). \(I_{sd}\) = the current flowing between the source and drain electrodes.

The transconductance is effectively a measure for the response intensity of a device, thus dividing the response by the transconductance results in a device-independent response. The use of device transconductance in nanosensors was first described by Ishikawa et al. on streptavidin-functionalized \(\text{In}_2\text{O}_3\)
nanowires. A similar approach was taken by Duan et al. for the comparison of silicon nanowires.

\[
\frac{\Delta G_{sd}}{g_m} = \Delta V_G
\]

Equation 6.2. Definition of \(\Delta V_G\). \(\Delta G_{sd}\) is the change in conductance between the source and drain electrodes, \(g_m\) is the device transconductance, \(\Delta V_G\) is the change in the backgate potential.

As \(V_G\) was kept constant (typically at \(V_G = 0\) V) Equation 6.2 effectively states that a change in the conductance of a GFET device divided by its transconductance yields a sensor response in the form of a change in the effective backgate potential \(V_G\). This change in the effective gate potential through the graphene is assumed to be the result of changes in the electric field through the graphene. In GFET devices that bind charged particles such as charged biomolecules the electric field near the graphene is modulated by the electric field caused by the discrete charge on the adsorbate. In the case of uncharged adsorbates the electric field is modulated by the dipole moment of the adsorbate that results from an uneven distribution of electron density in the adsorbate and its anisotropic distribution on the surface.

The ethene and carbonyl complexes of copper(I) bearing the \([\text{Tp}^{\text{CF3},4-\text{RPh}}]^{-}\) ligands were previously shown to have linearly predictable electronic properties. As their structures are highly similar their dipole moments were expected to follow a trend correlated to the \(\sigma_p\) parameters of the substituents on the ligands (this is discussed in more detail in section 6.2.6). The complexes should therefore influence the charge neutral point of graphene in a linear fashion if the following assumptions are true: the monolayer of molecules closest to the graphene causes the largest field effect and the molecules assemble in the same, or at least highly similar, orientations on the surface.

Unfortunately, as the larger GFET devices have large innate shifts of \(V_D\) away from 0 V the backgate potentials required to observe the Dirac points were higher than could safely be applied to the devices. In order to lower the required potentials it was necessary to shield the graphene from the substrate, this was achieved by insulating the substrate using octadecyltrimethoxysilane ((MeO)_3SiC_{10}H_{37}, OTS) which forms self-assembled monolayers (SAMs) of hydrophobic alkyl chains on the SiO_{2} surface. The alkyl chains provide distance between immobilized charges on the SiO_{2} surface and the graphene thus
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limiting their effect.\textsuperscript{[26]} To study the effect of these hydrophobic SAMs a control experiment was performed using a layer of the smaller trimethylsilyl (TMS) groups.

![Figure 6.9. The change in the Dirac point ($V_0$) of the OTS-functionalized devices as a function of the Hammett $\sigma_p$ parameters of the substituents on the phenyl rings of the [Cu(TpCF$_3$-4-RPh)(MeCN)] complexes.](image)

As expected the shorter spacing between the graphene layer and the SiO$_2$ substrate resulted in a larger residual effect of charge puddles as evident from the larger substrate-induced shift of the Dirac point (see Appendix VI). Using the OTS-modified substrates devices were fabricated that were characterized both before and after dip-coating with the copper complexes to find $\Delta V_0$ (see Figure 6.9). In all cases $\Delta V_0$ was found to have a positive value indicating that all complexes induced additional p-doping in the graphene. As the complexes are oxidatively quite stable, redox chemistry between the graphene and the complexes is unlikely to be responsible for the observed shifts in the Dirac points. Instead the p-doping effect is attributed to dipolar interactions with the graphene. Unfortunately, despite the predictable polarity of the complexes no correlation between the polarity of the complexes and the shift in the Dirac points was observed. Furthermore, a correlation between the layer thickness and $\Delta V_0$ was not observed. Differences in the exact orientation of the complex molecules on the graphene surface is therefore the most likely explanation for the lack of a predictable shift in the Dirac points of the graphene.
6.2.4. Detection of ethene and ethanol using the GFET devices.

The GFET devices were mounted on gas-tight epoxy chip carriers and placed in a Teflon flow cell that was tightly sealed using a poly(dimethylsiloxane) (PDMS) ring. Using two mass-flow controllers (MFCs) ethene gas (1% in synthetic air composed of 79% N₂ and 21% O₂) was further diluted with synthetic air to reach concentrations of 1, 0.5, 0.2 and 0.1 ppm, the range within which most climacteric crops respond to ethene exposure. The GFET devices were also exposed to ethanol which is an agriculturally relevant gas that signals rotting. As ethanol was expected to bind considerably more weakly to the copper(I) centers than ethene ethanol exposures were performed at 10, 5, 2 and 1 ppm. Data handling and processing is described in Appendix VI. As initial experiments showed large responses in the presence of atmospheric moisture all gas measurements were performed using dry gases. Desorption of water from the GFET surfaces most likely has the largest contribution to the drift of the baseline observed in these devices.

![Figure 6.10](image.png)

**Figure 6.10.** Responses of the GFET sensors comprising the sensitizing complexes [Cu(TpCF₃)ₓ(MeCN)] (R = NMe₂, OMe, H, F and Cl) or [Cu(TpCF₃)₂(MeCN)] upon exposure to different concentrations of ethene gas. Error bars indicate standard errors.

When the devices were exposed to ethene all of the sensors showed saturation at 1.0 ppm, except for the sensor bearing the reference complex [Cu(TpCF₃)₂(MeCN)] which showed a linear response in the entire range. In the cases of R = OMe or F saturation was even observed at 0.1 ppm. For ethanol the
devices showed signs of saturation at 10 ppm. As the required concentrations are quite low not all devices produced equally high quality data; drift in the baseline and poor signal-to-noise ratios occasionally obscured the signal. Nonetheless clear trends emerge when the responses of the sensors are collected (Figure 6.10). The complexes with electron-donating ligands (R = NMe₂, OMe and H) produce signals with a negative $\Delta V_0$ whereas the ligands with electron-withdrawing substituents (R = F and Cl) produce signals with a positive $\Delta V_0$.

**Figure 6.11.** Response intensities at saturation (calculated from the Langmuir fits, if no good Langmuir fit is available the signal at 1.0 ppm (C₂H₄) and 10 ppm (ethanol) was used) vs. the Hammett $\sigma_p$ parameters of the substituents on the hydridotrispyrazolylborate ligands of the copper(I) complexes. The ethene response of the device functionalized with [Cu(Tp₃CF₃,4-CF₃Ph)(MeCN)] marked with * is the actual signal with its sign reversed. Error bars indicate standard errors.

Contrary to expectations for [Cu(Tp₃CF₃,4-CF₃Ph)(MeCN)] the sensor produced a large negative signal ($\Delta V_0 = -202(9)\,\text{mV}$) when exposed to 1.0 ppm ethene gas, whereas ethanol exposures produced the expected positive signals (albeit of poor quality). The signal at 10 ppm ethanol exposure was $\Delta V_0 = 163(11)\,\text{mV}$ (the trace of the signal at 10 ppm ethanol exposures is shown in Appendix VI). The negative signal produced upon ethene exposure is surprising as the ellipsometry and AFM data showed no unusual surfaces for the [Cu(Tp₃CF₃,4-CF₃Ph)(MeCN)] functionalized devices compared to the other devices. In contrast,
the ethene and carbonyl complexes bearing the [Tp\textsuperscript{CF\textsubscript{3,4-CF\textsubscript{3}Ph}}] ligand were found to have predictable properties in NMR and infrared spectroscopy.\textsuperscript{[20]}

Particularly intriguing is the fact that if the sign of the negative signal is reversed the signal lines up very well with the values from the complexes with R = F and Cl (Figure 6.11). It appears plausible therefore, that [Cu(Tp\textsuperscript{CF\textsubscript{3,4-CF\textsubscript{3}Ph}})(C\textsubscript{6}H\textsubscript{4})] assumes a reversed orientation towards the graphene surface compared with the other ethene complexes resulting in a signal with a reversed (i.e. negative) sign.

6.2.5. Kinetics of ethene and ethanol sensing

When the GFETs respond reversibly, as they do after the first exposure to ethene gas, the reaction on the surface of graphene is assumed to consist of the conversion of a complex without associated ethene or ethanol, the “off” state and the ethene or ethanol complex, the “on” state as described in Scheme 6.2.

\[
[C\text{u}]_{\text{off}} + C_2H_4 \xrightarrow{k_1} \kappa \xrightarrow{k_1} [C\text{u}]_{\text{on}}
\]

Scheme 6.2. The equilibrium reaction between a copper(I) complex without associated ethene, the “off” state, and ethene forming the ethene copper(I) complex. \(k_1\) is the association rate constant and \(k_\kappa\) is the dissociation rate constant.

\[
\frac{\Delta G_{sd}}{\Delta g_m} = \Delta V_g = \frac{\Delta q}{C_0} [\text{on}]_{\text{max}} \times \frac{p(\text{an.})}{p(\text{an.}) + K_D}
\]

Equation 6.3. The relationship between the change in the conductance of the graphene and the output signal. \(\Delta q\) is the difference between the charges (in C) induced in the graphene by the dipole of the complexes in their “on” and “off” states. \(C_0\) (Fm\textsuperscript{-2}) is the coupling between the complexes and the graphene, \([\text{on}]_{\text{max}}\) is the maximum number of complexes in the “on” state per m\textsuperscript{-2}, \(p(\text{an.})\) is the partial pressure of the analyte gas (typically in ppm) and \(K_D\) is the equilibrium dissociation constant (in ppm) (\(K_D = k_\kappa / k_1\)).

The GFET surface consists of a discrete number of binding sites for analyte molecules (the copper(I) complexes) in a quasi-two-dimensional arrangement, as such it can be described using a Langmuir adsorption isotherm. The results of the gas-sensing experiments were therefore interpreted quantitatively by fitting Langmuir adsorption isotherms to the \(\Delta V_g/p\) plots (where \(p\) is the partial pressure of the analyte gas in ppm). The Langmuir isotherms used to describe the signals generated by the GFETs can be described using Equation 6.3.
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Equation 6.3 describes the generation of the signal $\Delta V_G$ as a function of the surface coverage of the graphene with the complexes that constitute the “on” state of the sensor, which are assumed to be the copper(I) ethene or ethanol complexes. The factor $\Delta q/C_0$ represents the change in the effective charge on graphene that is caused by the conversion of complexes in the “off” state to complexes in the “on” state. The first term, when multiplied by the maximum surface coverage with complexes in the “on” state, thus gives the maximum amplitude of the signal and is effectively a scalar (the coupling factor). The second term is the Langmuir adsorption isotherm that dictates the degree to which the graphene surface is covered in complexes in the “on” state. Equation 6.3 offers the possibility to extract the equilibrium dissociation constant $K_0$ and the term $(\Delta q/C_0)[\text{on}]_{\text{max}}$ that give insight into the importance of the contributions of the imposed charges on the graphene.

Aside from the equilibrium dissociation constant $K_0$ the (first order) dissociation rate constant $k_{-1}$ of the desorption of the analyte gases can be extracted from the traces of the gas sensing experiments. When fitting the dissociation phase of sensing experiments, care must be taken to consider both the dissociation and any possible re-association of the analyte, as molecules require time to diffuse away from the surface. This is particularly important when experiments are performed in solution as diffusion can be relatively slow. In this work the diffusion rates can be ignored, as rapid mixing is taken care of by application of a gas flow directly onto the sensor surface. Therefore, the kinetics of the dissociation can be modelled without considering the association rate constant $k_0$, leading to a simple exponential equation in which the signal decays from $V_{on}$ the potential during exposure, to $V_{off}$ the baseline signal (see Equation 6.4).

$$V_G = V_{on}e^{-k_{-1}t} + V_{off}$$

**Equation 6.4.** $V_{on}$ is the signal during analyte exposure, $V_{off}$ is the signal after dissociation of the analyte, $k_{-1}$ is the dissociation rate constant and $t$ is time.

Only the traces of the dissociation phase (immediately following the switch from gas exposure to synthetic air) could be fitted as the association events are obscured by large peaks resulting from the mass flow controllers (MFCs) (see Figure 6.12). The devices functionalized with the complexes [Cu(Tp$^{Gf3,4-RPS}(MeCN)] (R = \text{NMMe}_2$, H (ethene only), F (ethanol only) and Cl] showed signals with sufficiently good signal-to-noise ratios. Examples of fits using Equation 6.3 and Equation 6.4 are shown in Figure 6.13.
Physically returned to the baseline. The ethene concentrations were 20 ppm (1×), 1.0 ppm (3×), 0.5 ppm (3×), 0.2 ppm (3×) and 0.1 ppm (3×). The initial sharp peak is caused by the 20 ppm ethene flushing pulse. The other sharp peaks are caused by the MFCs. Inset: the same signal with the baseline subtracted clearly showing the saturation of the response at 0.1 ppm.

The equilibrium dissociation constants \( K_0 \), see Figure 6.14) were obtained for a number of the complexes and provide a clear distinction between the ethene and ethanol complexes. The equilibrium dissociation constants of the ethene complexes are 0.11(3) ppm (R = NMe₂), 0.23(3) ppm (R = H) and 0.21(7) ppm (R = Cl) while the values obtained for the ethanol complexes are considerably higher at 3(1) ppm (R = NMe₂), 3(1) ppm (R = F) and 4(1) ppm (R = Cl). Physically \( K_0 \) can be interpreted as the fraction of the analyte gas at which half of the copper complexes on the graphene surface are coordinated by analyte molecules.
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**Figure 6.13.** Examples of the fits used to determine $K_D$, $(\Delta q/C_0)\times V_{on,max}$ and $k_{-1}$ from the gas sensing experiments. Error bars indicate standard errors. **a)** The Langmuir adsorption isotherm fitted to the data observed when a non-OTS functionalized GFET sensitized with [Cu(Tp(CF$_3$)$_3$P)](MeCN) was exposed to ethanol. **b)** The fit obtained by fitting the dissociation of ethene from [Cu(Tp(CF$_3$)$_3$P)](C$_2$H$_4$) after exposure to 0.5 ppm ethene on a non-OTS GFET. The data in **a** and **b** were fitted using Equation 6.3 and Equation 6.4 respectively.

It is readily apparent that the GFETs can be exposed to higher concentrations of ethanol than of ethene before becoming saturated. There is no apparent correlation between $K_D$ and the Hammett $\sigma_p$ parameters of the substituents on the ligands in the complexes. The equilibrium dissociation constant of [Cu(Tp(CF$_3$)$_2$)](C$_2$H$_4$) and [Cu(Tp(CF$_3$)$_2$)](C$_2$H$_2$OH)] could not be determined but must be considerably higher than those observed in the other complexes as the response curve shows no signs of saturation at 1.0 ppm.

As the $K_D$ values are approximately equal for different complexes when they are exposed to the same gas it could be concluded that the scaling relation observed between $\sigma_p$ and $\Delta q$ is the result solely of the difference in the electronic effects of the complexes on the graphene. It is important to note that the complete absence of a correlation between the electron density on the copper(I) center and the $K_D$ of the ethene and ethanol complexes is physically impossible.
Figure 6.14. Equilibrium dissociation constants of ethene (red) and ethanol (black) on the GFETs as a function of the Hammett parameter of the substituent on the ligand of the sensitizer. Error bars indicate standard errors.

Figure 6.15. $k_1$ of the ethanol (black squares) and ethene (red circles) complexes vs. the Hammett $\sigma_p$ parameters of the substituents on the ligands. Error bars represent standard errors.

A trend in this regard should be most visible in the ethene complexes as the $\pi$-backbonding component of the Cu–C$_2$H$_4$ bond should help to enhance the effects of the electronic modification of the copper(I) center. Indeed in the
ethene complexes, although the effect is statistically insignificant, it appears that the \( K_0 \) for the complex with the most electron rich copper(I) center (\( R = \text{NMe}_2 \)) is smaller than the others.

The dissociation rate constants (\( k_{-1} \) in Equation 6.4, see Figure 6.15) were obtained from the traces of the dissociation phases of the gas exposure experiments. Both for the ethene and ethanol complexes the dissociation rate constants show a minimum at \( \sigma_p = -0.27 \) (\( R = \text{OMe} \)). For the ethanol complexes the experimental errors obscure whether or not both curves follow the same trend although this does appear to be the case. The rate of dissociation in the ethanol complexes is higher by a factor 1.5 – 2 in all cases. The \( K_0 \) and \( k_{-1} \) values observed for the ethene complexes and the ethanol complexes are listed in Table 6.1. As \( K_0 \) remains approximately stable irrespective of \( \sigma_p \) and \( K_0 = k_{-1}/k_1 \) \( k_1 \) must follow approximately the opposite trend.

### Table 6.1. \( K_0 \) and \( k_{-1} \) (10\(^{-3}\) s\(^{-1}\)) with standard errors.

<table>
<thead>
<tr>
<th></th>
<th>Ethene</th>
<th>Ethanol</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{NMe}_2 )</td>
<td>( K_0 ) (ppb)</td>
<td>( \pm )</td>
</tr>
<tr>
<td></td>
<td>110</td>
<td>34</td>
</tr>
<tr>
<td>( \text{OMe} )</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>3.9</td>
<td>0.03</td>
</tr>
<tr>
<td>H</td>
<td>230</td>
<td>26</td>
</tr>
<tr>
<td>F</td>
<td>9.9</td>
<td>0.08</td>
</tr>
<tr>
<td>Cl</td>
<td>208</td>
<td>66</td>
</tr>
</tbody>
</table>

\( \pm \) indicates standard errors.

As the MFCs could not be used to reliably produce concentrations lower than 0.1 ppm the lower limit of detection remains elusive. It is possible however, to estimate a limit of detection using the best peak-to-peak noise that was observed (in the OTS modified substrates) of 1 mV, and to extrapolate the performance of the \( \text{NMe}_2 \) substituted complex using the Langmuir isotherm fits for the ethene and ethanol detection experiments. Assuming a signal-to-noise ratio of at least 2 is required to identify a signal the extrapolated lower limits of detection are approximately 2 ppb for ethene and 35 ppb for ethanol. By using graphene with higher charge carrier mobility and thus lower levels of intrinsic noise these limits can be lowered further. Additionally peak-to-peak noise could be replaced by the RMS-noise which offers considerably better signal-to-noise ratios. With these improvements detection limits well below 1 ppb should be attainable for both ethene and ethanol.
The coupling factor \((\Delta q/C_0)[\text{on}]_{\text{max}}\) in Equation 6.3 can be extracted from the same fit as used for the equilibrium dissociation constants. This coupling factor determines the amplitude of the signal that is generated by the GFET upon exposure to the analyte. The coupling factors for the fitted curves are shown in Figure 6.16. The fitted coupling factors provide a number of interesting insights.

**Figure 6.16.** The value of the coupling factors \((\Delta q/C_0)[\text{on}]_{\text{max}}\) vs. the Hammett parameters \(\sigma_p\) of the substituents in the complexes [Cu(Tp\text{CF}_{3,4-Rp})(\text{MeCN})] that were used to sensitize the GFET devices.

Particularly, whereas the \(K_0\) values showed no correlation with \(\sigma_p\) the coupling factors do. The second observation is that the coupling factors for the ethene and ethanol sensing experiments are quite similar; apparently the induced changes in the effective charge of the complexes as felt by the graphene are not very different. The second observation can be nuanced by noting that at negative \(\sigma_p\) values (and thus more polar complexes) the values obtained for the ethene and ethanol sensing experiments drift apart indicating that either the dipole moments of the ethene and ethanol complexes do not scale the same way to \(\sigma_p\), or that the orientations of the complexes on the surface are not the same for all the complexes. The latter explanation is more plausible as the mechanism of assembly of the complex molecules on the graphene surface has a larger contribution from complex-complex interactions when the complex has a larger dipole moment. Changes in the exact orientation of the complexes on graphene would not only influence the projection of the dipoles on the graphene, but they might also change the stacking interactions between the complex and graphene.
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The exact contributions of each factor cannot be extracted from the data shown in Figure 6.16.

6.2.6. Mechanistic considerations

The electrical responses generated by the GFETs upon analyte exposure are the result of changes in the doping levels of the graphene caused by chemical changes in the copper complexes. In order to understand how the complexes induce such changes in the doping levels the surface chemistry of the GFET must be understood. Typically in GFETs the strongest signals are generated by direct charge injection into the graphene by analyte molecules, such as the generation of holes (oxidation) by NO₂. However, as the complexes used in this work are neither strongly reducing nor strongly oxidizing such a direct charge injection cannot be the mechanism by which doping levels are modulated.

Instead a more subtle mechanism such as modulation of the field effect by the dipole moments of the molecules must be responsible for the generated signals. As the dipole moment of a molecule has a direction depending on the geometry of the molecule any anisotropic arrangement of the molecules on the graphene surface will effectively result in the attraction or repulsion of charges in the graphene towards or away from the molecules.

The presence of strongly electron-withdrawing trifluoromethyl groups on the 3-positions of the ligands causes the dipole moments of their copper(I) compounds to range from very small when the phenyl rings are functionalized with electron-withdrawing groups (e.g. R = CF₃) to very large (R = NMe₂). As the orientation of the dipole vectors of the molecules with respect to the graphene surface influences the magnitude of the imposed electric field, the linear correlation between the factor Δq/C₀ and the Hammett σₚ parameters of the substituents on the ligands suggests that the complex molecules are similarly oriented with respect to the graphene surface. The notable exception is the GFET sensitized with [Cu(TpCF₃₄-CF₃P)(MeCN)] which generates a signal with the expected amplitude but the opposite sign.

To rationalize the obtained results it is instrumental to consider the structures of the complex molecules in their “on” and “off” states. The structures of the “on” states, after exposure of the GFETs to ethene, are assumed to resemble those of the structures determined with X-ray crystallography.[20] The structures of the ethanol complexes are not known but can reasonably be expected to be similar to those of the carbon monoxide or acetonitrile
complexes with the oxygen atom of the ethanol molecule coordinated to the copper center.

The exact identity of the "off" state complexes is less evident. The "off" state of a carbon nanotube-based device sensitized with [Cu(Tp\textsubscript{CF3})\textsuperscript{2}] was proposed to consist of a trigonal copper(I) complex in which one of the pyrazoles had dissociated from the copper(I) center in favour of coordination to the carbon nanotube. Such a structure may be the result of a local-minimum during calculations as its formation was found to be energetically highly unfavourable using DFT calculations.\textsuperscript{[4]} A more likely proposal in our eyes would be that the "off" state consists of species like the mononuclear 16-electron complex that forms upon dissociation of the analyte or its symmetric dimer.

![Scheme 6.3. Proposed mechanism for the detection of gaseous analytes. The irreversible loss of the acetonitrile ligand liberates the 16-electron complex which can then dimerize or react with ethene (or ethanol).](image)

Such a dimeric structure has not been reported with the ligand [Tp\textsubscript{CF3,Ph}]\textsuperscript{2} but crystal structures of such dimers have been reported for copper(I) scorpionate complexes such as [Cu(Tp\textsubscript{CF3,Me})\textsubscript{2}], [Cu(Tp\textsubscript{Ph,2})\textsubscript{2}], [Cu(Tp\textsubscript{Bu})\textsubscript{2}] and [Cu(Tp\textsubscript{Bu,Me})\textsubscript{2}].\textsuperscript{[27-29]} It has been reported that in solution the complex [Cu(Tp\textsubscript{Bu,Me})(MeCN)] exists in equilibrium with the dimer [Cu(Tp\textsubscript{Bu,Me})\textsubscript{2}] in \textsuperscript{1}H NMR only the acetonitrile complex and the dinuclear complex were observed.\textsuperscript{[27]} It can be concluded therefore, that in solution the interconversion between the mononuclear 16-electron species [Cu(Tp\textsubscript{Bu,Me})] and the dimer [Cu(Tp\textsubscript{Bu,Me})\textsubscript{2}] proceeds rapidly and nearly quantitatively. Evidence for the
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equilibrium between the mononuclear and dinuclear species in solution was found in all cases, it is therefore reasonable to assume that this equilibrium extends to the complexes used in this work.

To gain insight into the dipole moments of the complexes and the influence of the substituents on the ligands copper(I) complexes of the most electron-donating (R = NMe₂), the most electron-withdrawing (R = CF₃) and the ligand in between (R = H) were modelled using density functional theory at the ZORA-OPBE QZ4P level of theory. The calculated dipole moments show a clear distinction between the ethene and ethanol complexes and the mononuclear “off” states which have significant, predictable dipole moments and the dinuclear “off” state complexes which have dipole moments of nearly zero Debye (see Figure 6.17).

![Graph showing dipole moments vs Hammett σp parameters](image)

**Figure 6.17.** Dipole moments of the ethene (black), ethanol (red), mononuclear 16-electron (green) and dinuclear (blue) complexes as found for the structures of the complexes after geometric optimization using DFT (ZORA-OPBE/QZ4P, vacuum) vs. the Hammett σp parameters of the substituents on the hydridotrispyrazolylborate ligands.

The proposed mechanism shown in Scheme 6.3 relies on the conversion of the complexes in the “on” state to the dinuclear complexes. As evident from DFT calculations the dipole moments of the complexes show little change upon dissociation of the ethene or ethanol ligands. Only when the dinuclear species are formed the dipole moment becomes nearly zero. This result confirms the
hypothesis that the "off" state consists of the dimeric complexes rather than the mononuclear 16 electron complexes.

Figure 6.18. Optimized geometries for [Cu(TpCF3Ph)(C6H4)] (a), [Cu(TpCF3Ph)(C6H4OH)] (b), [Cu(TpCF3Ph)] (c) and [Cu(TpCF3Ph)]2 (d) and their dipole moments computed at the ZORA-OPBE/QZ4P level of theory in vacuum.

The expected trends are clearly visible; as the substituent R becomes more electron-donating the dipole moments of the complexes increase. The deviation from the expected line in the ethanol complexes is due to a distortion in the model caused by a hydrogen bond between the ethanol ligand and one of the fluorine atoms. This deviation is not observed in any of the gas sensing results and must be an artifact as the calculations were performed in vacuum. Additionally it is important to keep in mind that the exact structures, and thus their dipole moments, are affected by external forces such as packing effects on the graphene and π-stacking interactions between the complex molecules. The calculated values do show however, that the dipole moments of the molecules can be related to the Hammett σp parameters of the substituents on the ligands, which reinforces the impression that deviations from the trend in the gas sensing results are most likely due to differences in the exact orientations of the complex molecules on the graphene.
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6.3. Conclusions

We have successfully demonstrated the use of a series of copper(I) hydridotrispyrazolylborate complexes as sensitizers for a GFET based gas sensor. We showed that reproducible, homogeneous deposition of the copper complexes on graphene samples can be achieved using a simple dip-coating method and that the resulting layers have thicknesses of only a few monolayers. The use of device transconductance to adjust the output signals of the GFETs proved to be an effective method to remove device-dependent variations, which resulted in the observation of trends that can be related to the properties of the copper complexes. Cognizant of the observations from AFM, ellipsometry, gas detection experiments and DFT calculations we formed a complete image of the surface chemistry on the GFET devices, which we believe to be best described as a highly dynamic system wherein dinuclear complexes react with gaseous analytes through a coordinatively unsaturated mononuclear intermediate complex to form tetrahedral complexes with dipole moments that are dependent on the ligand used. The use of a Langmuir adsorption isotherm allowed for the extraction of $K_0$, $k_1$ and the coupling factors $(\Delta q/C_0)|_{\text{on}}$.

Somewhat surprisingly, the $K_0$ values of the ethene and ethanol complexes were found to depend only slightly on the electronic properties of the ligands. Indeed, variations in the amplitudes and the signs of the responses generated by the devices upon exposure to ethene and ethanol were found to scale with the dipole moments of the complexes with deviations from the predicted values resulting from differences in the orientations of the complexes on the graphene surface.

The GFET devices described here can be used for extremely sensitive detection of ethene at biologically relevant concentrations. The application of the complexes on a graphene surface using dip-coating provides a convenient handle for the fabrication of the devices on a larger scale. By integration into a single device of several graphene layers functionalized with different complexes the high sensitivity offered by some complexes can be combined with the larger range of sensitivity of other complexes to produce devices capable of highly sensitive detection in wide ranges of concentrations. We believe these devices can be used to great benefit in the reduction of the ethene-induced spoilage of fruits and vegetables during transport and storage and potentially represent one of the first real-world applications of graphene.
6.4. Experimental

6.4.1. General considerations

All manipulations of air-sensitive compounds were performed in an atmosphere of purified argon gas using standard Schlenk techniques. The synthesis of the sodium salts of the ligands was described previously.[20] All solvents were purchased from commercial sources and reagent grade. The graphene used in this work was purchased from Graphenea Inc. Solvents used for air-sensitive manipulations were dried and deaerated using a PureSolv MD 5 Solvent Purification System and stored on 3 Å molecular sieves under argon. When appropriate, glassware was flame dried in vacuo immediately prior to use. NMR spectra were recorded on a Bruker AV500 spectrometer (500 MHz for $^1$H, 471 MHz for $^{19}$F and 126 MHz for $^{13}$C). Elemental analyses were performed by the Microanalytical laboratory Kolbe in Germany. IR spectra were recorded on a Perkin Elmer UATR Two FT-IR spectrometer set to a resolution of 1 cm$^{-1}$. ESI-MS spectra of compounds in MeCN were recorded on a Thermal Finnigan AQA ESI-MS system. Contact angles were determined using a Ramé-Hart goniometer using drops of milli-Q water. Multiple drops were used and the results averaged. Ellipsometry was performed using a Vase Ellipsometer from J.A. Woollam Co. Inc. and fitted using a Cauchy model. Data analysis was performed using Origin 9.1 (OriginLab). AFM experiments were performed using a Nanoworld USC-F0.3-K0.3 tip in a JPK NanoWizard 4a NanoScience AFM. Calculations were performed with the Amsterdam Density Functional (ADF) software at the ZORA-OPBE/QZ4P level of theory in vacuum using the crystal structures of [Cu(Tp$_{CF_3,4R-9R}$)2(C$_2$H$_4$)] (R = NM$_2$, H and CF$_3$) and [Cu(Tp$_{Ph_2}$)$_2$]$_2$ or modified versions thereof as the initial structures.[20,28,30]

6.4.2. Lock-in technique

When used for ultrasensitive detection, the resistance change of the GFETs might be very small and overwhelmed by noise. In order to recover the very weak (and in our case very slow) sensing signal, we employed a lock-in amplifier (HF2LI, Zurich Instruments) to measure with very narrow bandpass filters (~1 Hz). We used the HF2LI to generate a sinusoidal alternating voltage (10 Vpk, frequency 10-100 kHz) to drive a sinusoidal alternating current through a 1 MΩ resistor (as a current source, 10 μA pk or 7.07 μA rms). This current source was connected to the GFETs (with resistances on the order of 1 kΩ) in series to drive a constant current $I_{sc}$ (7.07 μA rms) through the GFETs. The resultant voltage drop $V_C$ across the GFETs (proportional to graphene...
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resistance $R_{dc}=\frac{V_{dc}}{I_{dc}}$ was monitored versus time at a bandwidth of ~1 Hz using the ZiControl (Zurich Instruments) program. A noise frequency sweep was performed before every measurement to identify the testing frequencies with minimum noise power spectrum density (PSD), and thus optimizing the signal-to-noise ratio (SNR). A temperature sensor (Pt100) was mounted at the outlet of the gas tube and the gas temperature could be read off in-situ (experiments were conducted at room temperature).

6.4.3. Silanization of the wafer substrates

Si wafers with 288 nm SiO$_2$ were cleaned by rinsing with 2-propanol and milli-Q water. After being blown dry the substrates were immersed in a warm piranha solution for at least 60 minutes, rinsed with de-ionized water and dried at 150 °C for one hour. Thus cleaned, hydrophylized and dried the substrates were immersed in a 10% solution of trimethoxyoctadecylsilane (OTS, Sigma-Aldich, 90+%) in hexane and incubated at 60 °C overnight. For trimethylsilane (TMS) modification TMSI was used instead in combination with a few drops of ethyldiisopropylamine. The following day the substrates were rinsed sequentially using hexane, toluene, ethanol and water before being heated at 110 °C for at least one hour. The quality of the surface modifications was verified by sessile drop contact angle measurements which showed contact angles of ~100° for the OTS-modified surfaces and ~84° for TMS-modified surfaces.

6.4.4. Graphene deposition

The transfer of the chemical vapor deposition graphene films from Cu film to the substrate is done by first spin-coating a relatively thick PMMA (poly(methyl methacrylate)) layer over the graphene film on copper. After etching away any graphene that is not covered by the PMMA by oxygen plasma, the Cu film is dissolved in an ammonium persulfate solution. The solution is then completely exchanged multiple times with deionized water to remove as much of the dissolved salts as possible. Eventually, the graphene together with the polymer film is left floating in the aqueous phase from which it is carefully scooped up using a SiO$_2$/Si substrate. The PMMA film is dissolved using acetone, leaving uniform, large area monolayer graphene on the substrate for further processing. In order to remove residues left behind during the final washing step the graphene can be further cleaned by annealing in forming gas (8:2 Ar/H$_2$, 1-10 mbar, 80 sccm flow) at 350 °C for one hour. In case OTS-modified
substrates were used milder annealing conditions (160 °C, one hour) were used to preserve the OTS layers.

6.4.5. Device construction

Silicon substrates with graphene and Au electrodes were immersed for 10 minutes in 10 mM dichloromethane solutions of the copper complexes. The samples were then extensively rinsed using a stream of pure dichloromethane from a syringe before being blown dry in a stream of argon (Linde gas, 4.6 N) filtered through PTFE filter (pore size 0.45 μm) to exclude dust. The samples were annealed at 50 °C for 10 minutes and then immediately installed in the flow cell and flushed with air (200 sccm) for several hours to stabilize drift.

6.4.6. Synthesis of the copper(I) hydridotrispyrazolylborate acetonitrile complexes [Cu(Tp<sup>CF<sub>3</sub>,4CF<sub>3</sub>-Ph)(MeCN)]

General procedure

The sodium hydridotrispyrazolylborate (1.00 g, 1.14 - 1.38 mmol) was dissolved in dichloromethane (50 mL) or toluene (50 mL, only used in the case of NaTp<sup>CF<sub>3</sub>,4CF<sub>3</sub>-Ph) and the solution was purged with argon to remove dissolved dioxygen. After bubbling for five minutes [Cu(MeCN)<sub>4</sub>SbF<sub>6</sub> (1.0 equivalent) was added. The solution was left to stir under argon overnight. The following day the stirring was stopped to allow the NaSbF<sub>6</sub> by-product to settle. The supernatant was then siphoned off and filtered through a syringe filter (0.45 μm, PTFE). The clear solutions were evaporated to dryness in vacuo to yield the complexes as white solids. The complexes thus obtained were typically of good purity, additional purification could be performed by recrystallization of the complexes using DCM/Et<sub>2</sub>O, DCM/pentane or storage of a concentrated solution of a complex in DCM at −20 °C.

[Cu(Tp<sup>CF<sub>3</sub>,4CF<sub>3</sub>-Ph)(MeCN)]

Performed using half amounts of all compounds, yield 381 mg (87%). 1H NMR (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ 7.21 (d, <i>j</i> = 8.3 Hz, 6H), 6.98 (d, <i>j</i> = 8.3 Hz, 6H), 6.61 (s, 3H), 4.37 (bs, 1H), 2.32 (s, 3H). 19F NMR (471 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ −61.84, −63.48. 13C NMR (126 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ 148.66, 142.49 (q, <i>j</i> = 37.8 Hz), 134.68, 131.02 (q, <i>j</i> = 33.1 Hz), 130.46, 124.99, 124.13 (q, <i>j</i> = 272.0 Hz), 121.53 (q, <i>j</i> = 269.3 Hz), 114.55, 105.10, 1.16. Elemental analysis calculated (%) for C<sub>33</sub>H<sub>19</sub>BCuF<sub>18</sub>N<sub>7</sub>-1.5H<sub>2</sub>O-0.5Et<sub>2</sub>O (found): C 43.66 (43.36), H 2.67 (2.78), N 9.63 (9.36).
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\[ \text{Cu(Tp}^{CF3,4Cl,Ph})(\text{MeCN})/ \]
Yield 963 mg (95%). \(^1\text{H NMR} (500 \text{ MHz, CD}_2\text{Cl}_2) \delta 7.01 (d, J = 8.4 \text{ Hz, 6H}), 6.79 (d, J = 8.4 \text{ Hz, 6H}), 6.54 (s, 3H), 4.38 (bs, 1H), 2.30 (s, 3H). \(^{19}\text{F NMR} (471 \text{ MHz, CD}_2\text{Cl}_2) \delta -62.00. \(^{13}\text{C NMR} (126 \text{ MHz, CD}_2\text{Cl}_2) \delta 148.98, 142.20 (q, J = 37.4 \text{ Hz}), 135.09, 131.40, 129.56, 128.34, 121.61 (q, J = 269.4 \text{ Hz}), 114.41, 104.65 (q, J = 1.7 \text{ Hz}), 2.70. \]
Elemental analysis calculated (%) for \(\text{C}_{32}\text{H}_{19}\text{BCl}_{3}\text{CuF}_{9}\text{N}_{7}0.1\text{DCM} \)
(found): C 44.74 (44.48), H 2.25 (2.42), N 11.38 (11.18).

\[ \text{Cu(Tp}^{CF3,4F,Ph})(\text{MeCN})/ \]
Yield 635 mg (63%). \(^1\text{H NMR} (500 \text{ MHz, CD}_2\text{Cl}_2) \delta 6.87 (ddd, J = 8.2, 5.2, 2.5 \text{ Hz, 6H}), 6.73 (t, J = 8.7 \text{ Hz, 6H}), 6.52 (s, 3H), 2.30 (s, 3H). \(^{19}\text{F NMR} (471 \text{ MHz, CD}_2\text{Cl}_2) \delta -61.88, -113.25 (tt, J = 8.8, 4.7 \text{ Hz}). \(^{13}\text{C NMR} (126 \text{ MHz, CD}_2\text{Cl}_2) \delta 131.91 (d, J = 8.4 \text{ Hz}), 115.05 (d, J = 22.0 \text{ Hz}), 104.72 (q, J = 2.0 \text{ Hz}), 1.15. \]
Some resonances were not observed as a result of the low solubility of the compound and splitting caused by the fluoro substituents. Elemental analysis calculated (%) for \(\text{C}_{32}\text{H}_{19}\text{BCuF}_{12}\text{N}_{7}0.7\text{DCM} \cdot 0.1\text{Stolue}ne \)
(found): C 47.81 (48.22), H 2.70 (2.52), N 10.78 (10.37).

\[ \text{Cu(Tp}^{CF3,Ph})(\text{MeCN})/ \]
Yield 897 mg (87%). \(^1\text{H NMR} (500 \text{ MHz, CD}_2\text{Cl}_2) \delta 7.27 (dd, J = 8.1, 6.5 \text{ Hz, 3H}), 6.95 (t, J = 7.6 \text{ Hz, 6H}), 6.88 (dd, J = 7.9, 1.4 \text{ Hz, 6H}), 6.55 (s, 3H), 4.66 (bs, 1H), 2.30 (s, 3H). \(^{19}\text{F NMR} (471 \text{ MHz, CD}_2\text{Cl}_2) \delta -61.76. \(^{13}\text{C NMR} (126 \text{ MHz, CD}_2\text{Cl}_2) \delta 150.44, 141.94 (q, J = 37.3 \text{ Hz}), 131.07, 130.06, 128.61, 128.18, 121.83 (q, J = 269.0 \text{ Hz}), 114.32, 104.53 (q, J = 1.8 \text{ Hz}), 2.69. \]
Elemental analysis calculated (%) for \(\text{C}_{32}\text{H}_{22}\text{BCuF}_{6}\text{N}_{7} \)
(found): C 51.25 (51.11), H 2.96 (3.11), N 13.07 (12.73).

\[ \text{Cu(Tp}^{CF3,4Me,Ph})(\text{MeCN})/ \]
Yield 997 mg (97%). \(^1\text{H NMR} (500 \text{ MHz, CD}_2\text{Cl}_2) \delta 6.89 (d, J = 8.7 \text{ Hz, 5H}), 6.51 (d, J = 8.7 \text{ Hz, 6H}), 6.49 (s, 3H), 4.53 (bs, 1H), 3.78 (s, 9H), 2.29 (s, 3H). \(^{19}\text{F NMR} (471 \text{ MHz, CD}_2\text{Cl}_2) \delta -61.68. \(^{13}\text{C NMR} (126 \text{ MHz, CD}_2\text{Cl}_2) \delta 150.99, 150.40, 141.51 (q, J = 37.0 \text{ Hz}), 130.96, 122.00 (q, J = 268.6 \text{ Hz}), 118.83, 114.09, 111.44, 103.29, 40.17, 2.73. \]
Elemental analysis calculated (%) for \(\text{C}_{33}\text{H}_{28}\text{BCuF}_{6}\text{N}_{3} \)
(found): C 50.05 (49.99), H 3.36 (3.31), N 11.67 (11.61).

\[ \text{Cu(Tp}^{CF3,4Me,2,Ph})(\text{MeCN})/ \]
Yield 863 mg (84%). \(^1\text{H NMR} (500 \text{ MHz, CD}_2\text{Cl}_2) \delta 6.74 (d, J = 8.8 \text{ Hz, 6H}), 6.43 (s, 2H), 6.26 (d, J = 8.8 \text{ Hz, 6H}), 4.70 (s, 1H), 2.92 (s, 18H), 2.28 (s, 3H). \(^{19}\text{F NMR} (471 \text{ MHz, CD}_2\text{Cl}_2) \delta -61.61. \(^{13}\text{C NMR} (126 \text{ MHz, CD}_2\text{Cl}_2) \delta 160.07, 150.13, 141.80 (q, J = 37.3 \text{ Hz}), 131.46, 123.56, 121.86 (q, J = 268.8 \text{ Hz}), 114.26, 113.41, 103.97, 55.43, 2.70. \]
Elemental analysis calculated (%) for
C_{38}H_{37}BCuF_9N_{16.0.5}C_{6}H_{12} (found): C 53.15 (53.30), H 4.74 (4.26), N 15.30 (15.59).

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6.6. References

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