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Adsorption of TCNQH-functionalized quinonoid zwitterions on gold and graphene: evidence for dominant intermolecular interactions†

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We experimentally investigate the electronic structure of the strongly dipolar, quinonoid-type molecule obtained by TCNQH-functionalization (TCNQH = (NC)2CC6H4CH(CN)2) of (6Z)-4-(butylamino)-6-(butylimino)-3-oxocyclohexa-1,4-dien-1-olate C6H2(NHR)2(O)2 (where R = n-C4H9) to be very similar after deposition from solution on either graphene or gold substrates. These zwitterion adsorbate thin films form structures that are distinct from those formed by related quinonoid molecules previously studied. We argue that adsorbate–adsorbate interactions dominate and lead to a Stranski–Krastanov ‘island growth’ mechanism.

Introduction

A number of p-benzoquinonemonoimine zwitterion adsorbate thin films have now been investigated, using deposition from solution1–6 or from the vapour phase.6,7 These molecules were used as a model system for surface adsorption studies, taking advantage of their significant dipole moment of ca. 10 Debyes across a short distance, in order to gain a better insight into electrostatic contributions to surface adsorption phenomena. The chemical modification of the pendant groups attached to the nitrogen atoms (Fig. 1) also makes possible comparative studies of molecular thin films adsorption.2 In general, there is pronounced adlayer ordering, with a variety of molecular orientations and packing arrangements from upright1,2 to lying flat5–7 that depend on both the method of deposition and the substrate, owing to varying adsorbate-substrate interactions.5

Chemical modifications of the p-benzoquinonemonoimine zwitterions (see graphical abstract and the molecules of Fig. 1)

used in adsorbate thin films can lead to supramolecular assemblies6,8 (like that observed for tetracyanoquinodimethane (TCNQ))9–16 and possibly better hole-electron charge separation. The latter could significantly influence the exciton recombination rate, a key issue in organic solar cell optimization, and reports illustrate how the addition of dipolar molecules improves solar cell efficiencies.17–20

Fig. 1 The p-benzoquinonemonoimine zwitterions studied, including the dibutyl 1, the dibenzyl 2, the di(methoxybenzyl) 3, and the TCNQ-derived p-benzoquinonemonoimine zwitterion 4.

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Fig. 1 The p-benzoquinonemonoimine zwitterions studied, including the dibutyl 1, the dibenzyl 2, the di(methoxybenzyl) 3, and the TCNQ-derived p-benzoquinonemonoimine zwitterion 4.
Charge-assisted hydrogen bonding, which involves Coulombic interactions, is exceptionally appealing for molecular assembly and accounts e.g. for the remarkable properties of the charge transfer salts TTF (tetrathiofulvalene)-TCNQ (7,7,8,8-tetracyanoquinodimethane)\(^\text{21–26}\) and of the Bechgaard salts.\(^\text{25–29}\) It appeared to us attractive to functionalize the p-benzoquinonemonoimine zwitterion core by reaction with tetracyanoquinodimethane (TCNQ), which is one of the most widely used electron acceptors in organic solar cells. Adsorption of TCNQ and its derivatives on graphene and various metals has been widely studied,\(^\text{14–16,30–38}\) because of the presence of the four strongly electron-acceptor cyano groups with high electron affinity.\(^\text{38,39}\) For TCNQ, a p-doping of graphene results from a charge transfer of about 0.03 electron per C atom of graphene to the TCNQ adlayer.\(^\text{34}\) Furthermore, both theoretical and experimental analyses successfully showed that F4-TCNQ (i.e. tetrafluoro TCNQ) can open a band gap and induce p-type doping on graphene, with both the doping level and magnitude of the band gap being controlled by the thickness of the F4-TCNQ adsorbed layer.\(^\text{33,40–43}\)

Here we present experimental surface (spectroscopy) studies of TCNQH-functionalized p-benzoquinonemonoimine zwitterions aimed at investigating adlayers on graphene, using adsorption on Au for comparison. We show that these molecular films have properties distinct from those obtained with previously studied quinonoid zwitterions, with intermolecular interactions being stronger than the molecule-substrate interactions.

**Experimental methods**

The functionalized p-benzoquinonemonoimine zwitterions 1–3 were synthesized according to established procedures.\(^\text{4,44,45}\) The N-butyl-substituted zwitterion (6Z)-4-(butylamino)-6-(butylniminio)-3-oxocyclohexa-1,4-dien-1-olate \(C_6H_2(=\text{NHR})_2(=\text{O})_2\) (where \(R = n\text{-C}_4\text{H}_8\)) (1 in Fig. 1), was functionalized, as described before, by chemoselective insertion of TCNQ into the C–H bond of the O–C–CH–C–O moiety to give 4 with the moiety (NC)\(_2\)CC\(_6\)H\(_4\)CH(CN)\(_2\) as the C-substituent.\(^\text{46–48}\)

Graphene was grown on copper foil by Chemical Vapor Deposition (CVD) at 1000 °C, at the pressure of 1.4 Torr for 30 min using the gas mixture of C\(_2\)H\(_2\) (1.4 sccm) and H\(_2\) (2 sccm). The zwitterions were deposited on clean gold and graphene substrates from a CH\(_2\)Cl\(_2\) solution, as noted in prior work.\(^\text{1,2,4}\)

Combined photoemission (UPS) and inverse photoemission (IPES) studies were performed on molecules deposited on gold or graphene. The spectra were taken in a single ultrahigh vacuum chamber to study the placement of both occupied and unoccupied molecular orbitals of the quinonoid zwitterion, as was done in prior work.\(^\text{1,2,4}\) Experiments were performed with the electron emission (photoemission) or electron incidence (inverse photoemission) along the surface normal to preserve the highest symmetry. In both cases, the binding energies are referenced to the Fermi edge of gold or copper, as appropriate, and the data are expressed in terms of \(E - E_F\) (thus making occupied state energies negative). Film thickness and film uniformity were determined using atomic force microscopy (AFM) and core level X-ray photoemission (XPS), as in prior work with various adsorbed p-benzoquinonemonoimine zwitterions.\(^\text{2}\)

**Modeling**

Calculations of the occupied and unoccupied molecular orbitals of molecular films were performed for comparison purposes with the density of states deduced from the UPS-IPES experiments. As in previous studies,\(^\text{1–4}\) the orbital energies of the single molecules (as in a gas phase experiment) were calculated using the neglect of differential diatomic overlap NDO-PM3 (neglect of differential diatomic overlap, parametric model number 3) based on Hartree–Fock formalism. Geometry optimization for each of the zwitterions was performed by obtaining the lowest restricted Hartree–Fock energy states. The density of states (DOS) were modelled by applying equal Gaussian envelopes of 1 eV full width half-maximum to each molecular orbital, to account for the solid-state broadening in photoemission, and then summing over each Eigen state. This model density of states calculations were rigidly shifted in energy, largely to account for the influence of the work function on the orbital energies and no correction was made for molecular interactions and final state effects. This is schematically indicated in Fig. 2, where the molecular orbital offsets are schematically illustrated for the methoxybenzyl-functionalized zwitterion \(C_6H_2(=\text{NHR})_2(=\text{O})_2\), where \(R = -\text{CH}_2-\text{C}_6\text{H}_4-\text{OCH}_3\) (3 in Fig. 1) relative to the single molecule orbital calculations calculated by PM3 and the density functional theory (DFT). No correction was made for matrix element effects or light polarization and comparison with experiment requires caution as both photoemission and inverse photoemission are final state spectroscopies and the eigenvalues are from a ground state calculation.

**Results**

The methoxybenzyl-functionalized zwitterion \(C_6H_2(=\text{NHR})_2(=\text{O})_2\), where \(R = -\text{CH}_2-\text{C}_6\text{H}_4-\text{OCH}_3\) (schematically shown as 3 in Fig. 1), shows a significantly different placement of the lowest unoccupied molecular orbital (LUMO) when absorbed on gold (Fig. 3a) versus graphene (Fig. 3b), as previously observed for other p-benzoquinonemonoimine zwitterions.\(^\text{4}\) The energy states of the conduction band edge, related to the LUMO, are placed much closer to the Fermi level for 3 deposited on gold than on graphene (Fig. 3). The placement of unoccupied molecular orbitals for 3 on graphene is in reasonable agreement with expectations from the ground state single molecule orbital energies based on the semiempirical PM3 methodology (Fig. 2b and 3c). For 3 deposited on gold, a much better agreement is obtained with model ground
state calculations based on a smaller highest occupied molecular orbital (HOMO) to lowest unoccupied molecular orbital (LUMO) gap that would be something like a combination of the semiempirical PM3 and density functional theory calculations (Fig. 2b). This is in general consistent with the expectation that zwitterions 1 and 3 both interact weakly with graphene compared to gold. The extent of adsorbate molecule to substrate interaction does matter: if the interactions of the molecular adsorbate with the substrate are too weak, then intermolecular interactions may dominate. When the intermolecular interactions are much stronger than the molecule-substrate interactions, then “wetting” of the substrate with the adsorbate layer is less likely to be energetically favorable. In that case, as long as there is little kinetic hindrance, i.e. diffusion of molecules across the surface is possible, then a Volmer–Weber island growth mechanism of the molecular film should be expected.

For the TCNQH-functionalized zwitterion 4, the HOMO (highest occupied orbital) to LUMO gap that would be something like a combination of the semiempirical PM3 and density functional theory calculations (Fig. 2b). This is in general consistent with the expectation that zwitterions 1 and 3 both interact weakly with graphene compared to gold. The extent of adsorbate molecule to substrate interaction does matter: if the interactions of the molecular adsorbate with the substrate are too weak, then intermolecular interactions may dominate. When the intermolecular interactions are much stronger than the molecule-substrate interactions, then “wetting” of the substrate with the adsorbate layer is less likely to be energetically favorable. In that case, as long as there is little kinetic hindrance, i.e. diffusion of molecules across the surface is possible, then a Volmer–Weber island growth mechanism of the molecular film should be expected.

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This is accompanied by a decrease of the HOMO–LUMO gap, at variance with observations made with zwitterion 1.4

Strong intermolecular interactions between molecules of 4 are consistent with the measured decrease of the HOMO–LUMO gap with increasing molecular film coverage. Model pairwise calculations on 4, as a function of intermolecular distance, typically show a decrease in the HOMO–LUMO gap energies, as indicated in Fig. 5. This is just representative of the pairwise interactions: a number of different molecular orientations lead to the same qualitative result: the HOMO–LUMO gap decreases with decreasing intermolecular spacing.

Fig. 5 Comparison of the HOMO–LUMO gap as a function of intermolecular spacing for a pair of TCNQ-derived p-benzoquinonemonoimine zwitterions (4) (the cif file of the crystal structure of 4 is available from CCDC 830133).46 A number of different molecular orientations lead to the same qualitative result: the HOMO–LUMO gap decreases with decreasing intermolecular spacing.

The attenuation of the X-ray photoemission substrate signal from the (a) gold (Au 4f core levels) and (b) graphene on copper (the Cu 3p core levels) substrates. The core level spectra are shown for clean gold (blue), and the substrates following adsorption of 1 to 2 molecular monolayers of zwitterion 4 on gold (a) and graphene on copper (b) (shown in red). Much thicker molecular films create islands of zwitterion 4 molecules (Fig. 5) but do not suppress more than 15–30% of the substrate X-ray photoemission signal (black).

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Fig. 6 The attenuation of the X-ray photoemission substrate signal from the (a) gold (Au 4f core levels) and (b) graphene on copper (the Cu 3p core levels) substrates. The core level spectra are shown for clean gold (blue), and the substrates following adsorption of 1 to 2 molecular monolayers of zwitterion 4 on gold (a) and graphene on copper (b) (shown in red). Much thicker molecular films create islands of zwitterion 4 molecules (Fig. 5) but do not suppress more than 15–30% of the substrate X-ray photoemission signal (black).
withdraw electron density from graphene,\textsuperscript{38,39} this does not prevent the TCNQH-functionalized zwitterion 4 from donating electron charge to the graphene.

Island growth of the zwitterion 4 on both gold and graphene on copper is apparent from the AFM images (Fig. 7). The clear tendency for these molecules to form clusters or islands results from intermolecular interactions that are far stronger than those with the graphene or gold substrates. We shall come back to this point later. The observed islands of 200 nm (on gold) and 150 nm (on graphene) in height do not obscure the substrates gold or copper X-ray photoemission core level signals (Fig. 6). The fact that the core level shift is uniform suggests that the TCNQH-functionalized zwitterion 4 on gold does cover the surface at low coverage and then adopts island growth at high coverage. This suggests a Stranski-Krastanov\textsuperscript{52,53} rather than a strict Volmer-Weber growth mode.\textsuperscript{53} The critical layer thickness at the onset of island formation cannot be ascertained from our measurements here, but the very large substrate signal evident in the XPS data is indicative of the formation of a very thin (1–3 nm) molecular overlayer before island growth is initiated.

The crystal packing of the TCNQ-derived \textit{p}-benzoquinonemonoimine zwitterion 4, first described in prior work,\textsuperscript{46–48} presents multiple opportunities for strong hydrogen bonding, as illustrated in Fig. 8. Head-to-tail arrangement of two adjacent molecules is favored (Fig. 8a), as expected from dipolar electrostatic interactions and as observed with most members of the family of functionalized zwitterions. The TCNQH group provides additional possibilities for intermolecular hydrogen bonding with one proton of the butyl pending group (Fig. 8b). There are also hydrogen bonding interactions between the CN groups and aromatic protons of the TCNQH moiety of adjacent molecules (Fig. 8c). Such a wealth of hydrogen bonding should lead to intermolecular interactions stronger than commonly found with the non-functionalized quinonoid zwitterions and contribute to the type of molecular film growth seen here.

**Conclusion**

When deposited on graphene or gold, the TCNQH-functionalized \textit{p}-benzoquinonemonoimine zwitterion 4 favors an island growth morphology. The electronic structure seen in photoemission and inverse photoemission reveals limited molecule-substrate interactions and suggests strong intermolecular interactions. The latter are consistent with the known crystalline structure of 4, which reveals more hydrogen bonding interactions than for other quinonoid zwitterions previously investigated. The XPS studies of adsorption on gold favor a model of very thin initial molecular thin film coverage, prior to island growth, \textit{i.e.} of Stranski-Krastanov growth type.

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**References**

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The orbital energies with respect to the vacuum level using the semi-empirical PM3 model for

a) methoxybenzyl-functionalized zwitterion $C_6H_2(\cdots\text{NHR})_2(\cdots\text{O})_2$, where R = -CH$_2$-C$_6$H$_4$-OCH$_3$:

-0.38799  LUMO (+2)
-0.46374  LUMO (+1)
-2.11035  LUMO (0)
-7.57282  HOMO (0)
-9.01096  HOMO (-1)
-9.10518  HOMO (-2)

b) TCNQH-functionalization (TCNQH = (NC)$_2$CC$_6$H$_4$CH(CN)$_2$) of (6Z)-(4-(butylamino)-6-(butyliminio)-3-oxocyclohexa-1,4-dien-1-olate $C_6H_2(\cdots\text{NHR})_2(\cdots\text{O})_2$) (where R = n-C$_4$H$_9$):

-0.54888  LUMO (+2)
-0.73256  LUMO (+1)
-3.736    LUMO (0)
-8.60307  HOMO (0)
-9.53232  HOMO (-1)
-9.65609  HOMO (-2)