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Charge-transfer complexes interactions evidenced by chemical force microscopy

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Charge-transfer complexes have been detected by chemical force microscopy (CFM) between a tip and a substrate respectively functionalized with trinitrofluorenone and 9-anthracenemethanol siloxane derivatives.

The formation of charge-transfer complexes (CTC) between two aromatic compounds has been the subject of much research over the last thirty years. These complexes have been used in analytical applications (chromatographic separation),[1] and have also been involved in biological systems for molecular recognition.[2] Furthermore, selective organic transformations have been controlled by donor–acceptor interactions,[3] CTC molecular clips have been used in supramolecular chemistry,[4] and also tested for an industrial application in the purification of gas oils.[5]

We have assumed that this reversible complex formation ought to be detectable by atomic force microscopy (AFM). Indeed, this direct and sensitive force measurement method[6] (also known as chemical force microscopy, CFM) has already been successfully used to allow discrimination between enantiomers of simple chiral molecules,[7] or to detect individual supramolecular host–guest interactions.[8] Most of the examples are however to be found in investigations for measurements of biological interactions.[9,10] The main advantage of AFM spectroscopy, as a non destructive tool, relies on the direct measurement of the adhesion forces acting between the modified tip and a modified surface, thus enabling to information to be obtained on the binding energy in the sub-nanonewton range.

We were thus interested to test AFM as a technique to evaluate the chemical binding force of charge-transfer complexes formed at the interface between an electron-deficient compound, covalently bonded to the tip and an electron-rich modified surface. As we started this study, there was, to the best of our knowledge, no report in the literature dealing with the detection of such interactions by AFM. Very recently however, Skulason and Frisbie[11] published the successful measurement of the chemical binding forces of discrete CTC between gold-coated tips and substrates through alkane thiol self-assembled monolayers. They were able to measure pull-off forces between modified tips and substrates in chloroform and to propose a 70 pN force assigned to the rupture of individual CTC.

We measure here by AFM spectroscopy[12] the binding force between charge-transfer complexes formed between a tip modified with a trinitrofluorenone derivative (**1**) and a cover glass surface modified with a 9-anthracenemethanol derivative (**2**). Both acceptor and donor molecules were covalently bonded to the supports *via* chemical reaction of trialkoxysilanes, as depicted in Fig. 1.

Electron donor–acceptor complexes are easily detected by UV-Vis spectroscopy because their formation is generally accompanied by the appearance of a new absorption band (Benesi–Hildebrand band).[13] Following the method of Foster–Hammick–Wardley,[14] this phenomenon allows the calculation of the association constant characterizing the complex. 2,4,7-Trinitrofluorenone and anthracene were selected due to their good solubility in chloroform to model the formation of charge-transfer complexes in solution. Indeed, a mixture of these compounds in $CHCl_3$ gave rise to a new absorption wave (λ_{max} 538 nm) corresponding to the calculation of an equilibrium constant of 11.5 Lmol^{-1} at room temperature and of the extinction coefficient of the complex ε_{358} = 770 Lmol^{-1} cm^{-1}. The results above show that CFM technique should be sensitive enough to detect a CTC formation with an estimated free energy around -6 kJ mol^{-1}.

The 9-oxo-2,5,7-trinitro-9*H*-fluoren-4 carboxylic acid[15] was transformed through an amidation reaction with 3-aminopropyltrimethoxysilane in the presence of DCC to afford the corresponding silylated derivative (**1**) in 69% yield. Accordingly, 3-triethoxypropylisocyanate was used to prepare the silylated carbamate derivative of 9-anthracenemethanol (**2**) in quantitative yield. The tip[16] and the sample were prepared by immersion for 4 hours at room temperature in toluenic solutions (around 0.08 M) of these siloxane derivatives. Pull-off forces were then measured in two solvents, *i.e.* dodecane and 1-methylnaphthalene, in which CTC binding forces were assumed to be different. A series of 300 experiments was performed in dodecane with a velocity of 5 to 10 nm s^{-1}. Each force curve was described by 2000 datapoints. The obtained binding forces are represented as a histogram in Fig. 2A, with an average value of 6.6 nN ± 3.5 nN.

Under similar experimental conditions, the tip-surface pair was examined in 1-methylnaphthalene as non-volatile aromatic solvent, acting as a competitor for the anthracene derivative (**2**) towards the formation of CTC with the nitrated fluorenone (**1**) compound. The observed binding forces are significantly reduced compared to those measured in dodecane (see Fig. 2B) with an average value of 1.7 nN ± 0.5 nN. This fact strongly

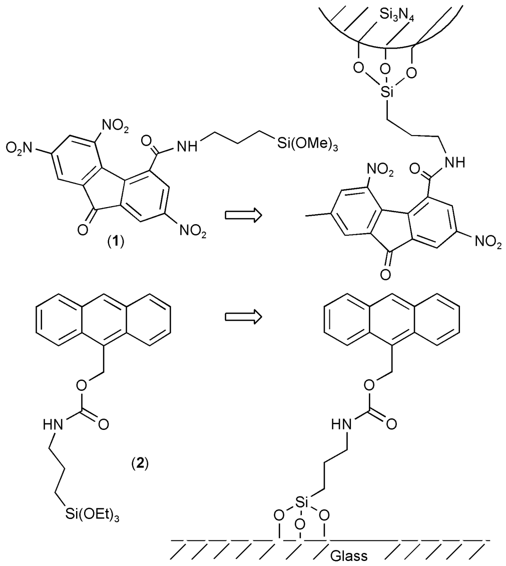

Fig. 1 Representation of the modified tip and surface to measure CTC.

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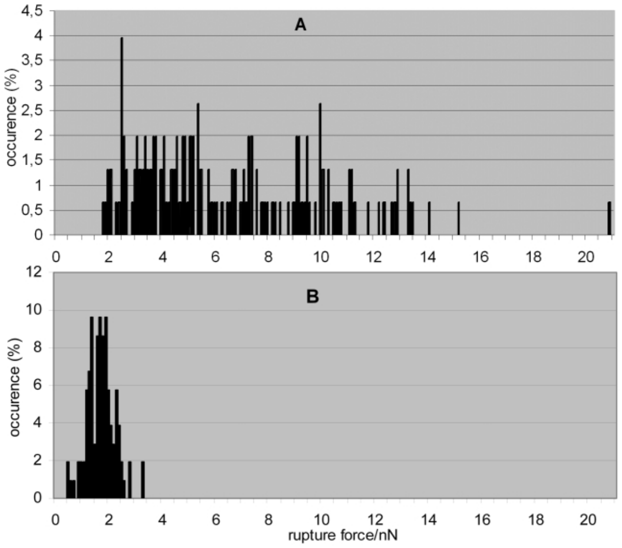

Fig. 2 Histograms of pull-off forces for an AFM tip modified with (**1**) on a surface modified with (**2**) in A) dodecane or B) 1-methylnaphthalene.

suggests that the specific interactions measured in dodecane arise from the formation of charge-transfer complexes between the molecules covalently tethered to the probe tip and substrate. In 1-methylnaphthalene, in which the formation of donor–acceptor complexes between anthracene and trinitrofluorenone is highly disfavoured, only smaller residual interactions were detected. After replacement of the aromatic solvent by dodecane, strong interactions were again measurable, with an average force of 10.0 nN ± 3.9 nN, indicating that the phenomenon was, as expected, totally reversible. Further control experiments were run in dodecane, in which a tip functionalized with the electron-deficient compound was brought into contact with a non-modified probe. The corresponding force–distance curves showed pull-off events characteristic of weak, residual interactions (0.5 nN ± 0.5 nN).

Dynamic experiments were moreover carried out to study the effect of the velocity of the tip/sample separation on the observed adhesion forces. Pull-off forces were measured at different scan rates, varying from 0.01 s to 100 s for a 750–1200 nm distance between the functionalized tip and substrate in dodecane. As evidenced in Fig. 3, the time used to carry out a complete contact/separation cycle has no influence on the CTC force, with an average value of 7.9 nN ± 2.1 nN, under those conditions. A saturated solution of anthracene in dodecane was then used as solvent, to study the effect of a free competitor on the measured adhesion forces. Pull-off forces were again measured at different sweep times, leading as a whole to specific forces weaker than those measured without competitor. In this case however, the scan rate influenced markedly the measured forces between the tip and the substrate. When the contact/separation was performed in less than one second, only low interactions could indeed be measured. We propose that under those experimental conditions, charge-transfer complexes were rapidly formed between the "electron-deficient tip" and free anthracene in solution, acting here as a poison for the tip. Furthermore, with increasing sweep duration (higher than 1 s), the observed specific forces between the tip and the sample became stronger. A long enough contact time probably allows an exchange between the complexes formed with anthracene in solution and with the donor covalently bonded to the surface by the siloxane functionality.

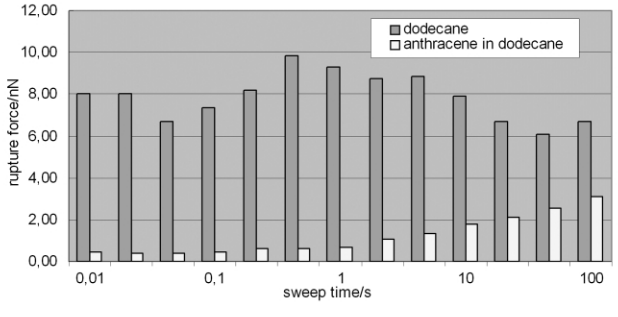

Fig. 3 Histogram of pull-off forces recorded during dynamic experiments at different sweep times, in dodecane without and with anthracene as competitor.

To conclude, we have successfully functionalized a tip and a probe with an electron-deficient and an electron-rich compound, respectively, using siloxane derivatives, a support-modification rarely used for AFM measurements. In dodecane, pull-off forces were evidenced, characteristic of the formation of charge-transfer complexes between the tip and the substrate, since they strongly decreased in 1-methylnaphthalene as an inhibiting aromatic solvent. Competitive dynamic experiments, carried out with anthracene dissolved in dodecane, led to pull-off forces values dependent on the sweep rate. At long sweep duration (higher than 1 s) higher pull-off forces (2.0 nN ± 1.0 nN) were measured than at shorter sweep time (less than 1 s, 0.6 nN ± 0.3 nN). We propose, that the longer the contact time, the more efficient are exchanges between free- and bonded-anthracene or more probable is the diffusion of free anthracene molecules outside the contact area. From these encouraging preliminary results, we assume charge-transfer complexes to be investigated by AFM contact/separation technique. We are currently working on the application of this method to the study of other CTC systems and the extension to other interactions in the catalysis field.

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16 200 μm long thin legged, V-shaped silicon nitride cantilevers with pyramidal unsharpened tip "Nanoprobe" from Digital Instruments were used (force constant 0.06 N m^{-1}).