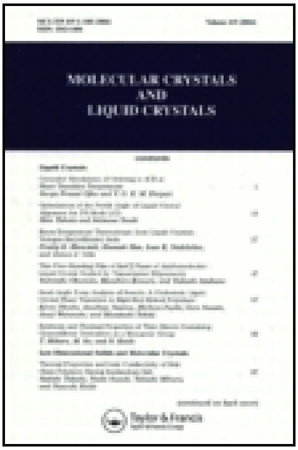

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Self-Assembled Monolayers of 1,10-Phenanthroline Based Bis-Bidentate Ligands on Au(111)

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Version of record first published: 31 Aug 2012.

To cite this article: François Lux, Gilles Lemercier, Chantal Andraud, Guillaume Schull & Fabrice Charra (2008): Self-Assembled Monolayers of 1,10-Phenanthroline Based Bis-Bidentate Ligands on Au(111), Molecular Crystals and Liquid Crystals, 485:1, 881-886

To link to this article: http://dx.doi.org/10.1080/15421400801922726

Mol. Cryst. Liq. Cryst., Vol. 485, pp. 133/[881]–138/[886], 2008
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ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400801922726

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Self-Assembled Monolayers of 1,10-Phenanthroline Based Bis-Bidentate Ligands on Au(111)

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The possibility for two bis-bidentate polypyridyle type ligands (TPPHZ and PEP) to form Self-Assembled Monolayers (SAMs) on Au(111) surfaces, has been investigated by Scanning Tunelling Microscopy (STM).

Keywords: 1,10-Phenathroline; self-assembled monolayers; STM

INTRODUCTION

Molecular self-assembly at well-defined surfaces emerges as a new bottom-up tool for the fabrication of nanostructures and patterns on the nanometre scale [1]. It is based on a spontaneous ordering of molecules governed by the interplay between molecule-molecule and molecule-substrate interactions. Scanning tunnelling microscopy (STM) at the liquid/solid interface is one of the preferred techniques to investigate the organisation and properties of the self-assembled monolayers (SAMs) [2]. The most studied system on gold and silver surfaces is undoubtedly alkanethiols. It consists in a dense brush-like monolayer with lateral organisation driven by the sites favourable for sulphur-gold bonding [3]. Unfortunately, whereas control of the lateral assembly is one of the prerequisites for observation and potential applications in the fields of nanoscience and nanotechnology, the size increase of the thiol-functionalized molecules leads to poor and even no lateral order [4].

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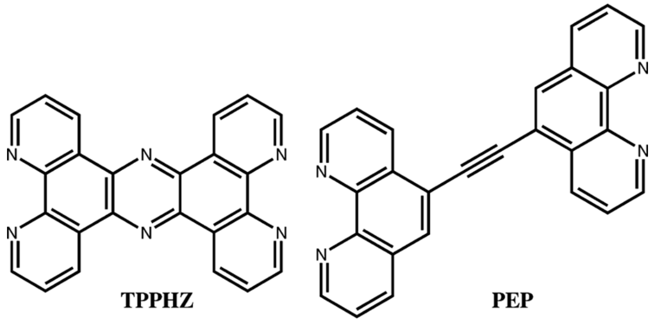


FIGURE 1 Molecular structures of TPPHZ and PEP.

2,2′-bipyridine [5], 1,10-phenanthroline [6], or oxadiazole derivatives [7] form edge-on π-stacked assemblies on Au(111), providing evidences for the strong interaction of the chelate species with Au(111) surfaces. In a recent study, we extended this observation to the case of the substituted 1,10-phenanthroline derivatives: a long alkyl chain was grafted on the 1,10-phenanthroline [8] according to a modified Sonogashira reaction [9]. This derivative (DYP) was deposited on highly oriented pyrolitic graphite (HOPG) and Au(111) and investigated by STM. The self-assembly on graphite followed the standard paradigm of molecules lying flat on the surface [10], bonded to HOPG through the adsorption of the alkyl chain in registry with graphite. On Au(111) substrate, a quite different alignment of upright-oriented molecules was formed, which has been explained by a decreased adsorption energy of the alkyl chains and an increased interaction of the chelate moiety with the surface.

These results have demonstrated the possible formation of an intermediate type of bonding combining a brush like geometry with a controlled lateral organization. The next step, reported hereafter, will consist in the study of the self-assembling of bis-bidentate ligands derived from the 1,10-phenanthroline TPPHZ and PEP (see Fig. 1). These ligands are well suited for this study and lateral stabilisation, because of their rigid and large aromatic core; they are expected to enable the functionalization of gold surfaces leaving an idle polypyridyl function for subsequent complexation.

EXPERIMENTAL SECTION

^{1}H and ^{13}C NMR spectra were recorded on a Brücker AC200 spectrometer (at 200.13 MHz for ^{1}H and 50.32 MHz for ^{13}C). Melting points m.p. were recorded on a Perkin Elmer DSC7 micro-calorimeter.

Elemental analysis were carried out by the Service Central d'Analyse CNRS at Solaize. Tetrapyridol[3,2-a:2′,3′-c:3″,2″-h:2‴,3‴-j]phenazine (TPPHZ) was synthetized according to a procedure already described in the litterature [11].

Synthesis of 5-(5-[1,10-phenanthrolinyl]-ethynyl)-1,10-phenanthroline (PEP). A solution of 5-bromo-1,10-phenanthroline [12] (1.5 g, 5.8 mmol), trimethylsylilacetylene (0.85 g, 8.7 mmol) and tetrakis-(triphenylphosphine)-palladium(0) (330 mg, 2.9 mmol) in pyrrolidine (20 mL) was stirred under argon at 80°C overnight in a closed reactor. 220 mg of a pale orange solid was obtained by filtration and washed with pentane (20% yield). ^{1}H NMR (200.13 MHz; $CDCl_3$): δ (ppm): 9.29 (1H, dd, H_2 or H_9, $J = 4.3$; 1.7 Hz); 9.24 (1H, dd, H_9 or H_2, $J = 4.3$; 1.7 Hz); 8.93 (1H, dd, H_4, $J = 8.2$; 1.7 Hz); 8.30 (1H, dd, H_3 or H_8, $J = 8.2$; 4.3 Hz); 8.28 (1H, s, H_6); 7.80 (1H, dd, H_8 or H_3, $J = 8.2$; 4.3 Hz); 7.69 (1H, dd, H_8 or H_3, $J = 8.2$; 4.3 Hz). Anal. Calcd for $C_{26}H_{14}N_4$ 0.66 H_2O: C 79.17 N 14.20. Found: C 79.21 N 14.19.

STM imaging. The STM was operated at the liquid–solid interface. Nearly-saturated solutions of either PEP or TPPHZ in *n*-tetradecane (>99%, Aldrich) or phenyloctane have been used. These solvents are well adapted for *in-situ* scanning tunneling microscopy (STM) because they are hydrophobic, electrically highly-insulating and exhibit low vapor pressure. The STM junction was immersed in a droplet of solution immediately before STM scanning. The substrates were 100-nm-thick layers of gold epitaxially grown on mica following known procedures so as to expose a (111) face [13]. The substrates were flame annealed immediately before their use. The observation of the $22 \times \sqrt{3}$ reconstruction in the pure solvent was a prerequisite for further use of each substrate. The tips were mechanically formed in a 250-µm Pt-Ir wire (Pt80/Ir20, Goodfellow). STM imaging was achieved through an home-made digital system, specially designed for low-current operation. The images reported here were obtained in the height (also called "constant current") mode.

RESULTS AND DISCUSSION

For solubility issues, phenyloctane was used as the solvent in the experiments with the TPPHZ. Immediately after application of the droplet, small islands of parallel strips were observed (Fig. 2). The strip-to-strip lateral period is ~1.6 nm. This value is larger in comparison with the DYP ligand length (~0.9 nm). The apparent height of these patterns relative to the naked gold surface is larger than 1.5 Å.

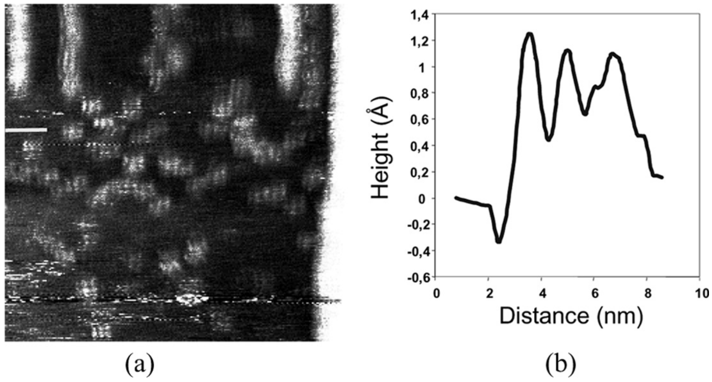
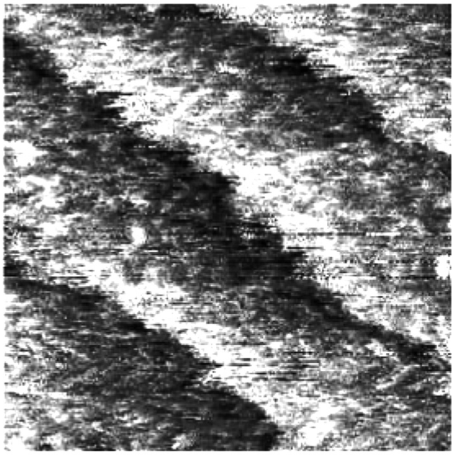


FIGURE 2 (a) STM image of TPPHZ on Au(111). The image size is 76 nm × 76 nm. The tunnelling current was $I_T = -20$ pA, and the sample bias was $V_S = -1.5$ V. (b) Height cross-section along the line displayed in the image.

Nearly full coverage is observed after several hours of exposure to the solution (Fig. 3), but there is a loss of organization concurrently to the densification of the monolayer. A change of organization

(a)



(b)

FIGURE 3 (a) STM image of TPPHZ after 1 h exposure to the solution. The image size is 20 nm × 4 nm. (b) STM image of TPPHZ after 2.5 h of exposure to the solution. The image size is 20 nm × 20 nm.

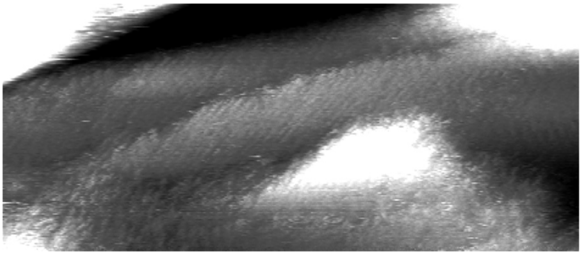


FIGURE 4 PEP on Au(111) after a night of exposure to the solution. The image size is 42 × 17 nm.

improving the coverage is often observed as a response either to a prolonged exposition or to an increased solution concentration. This is the case in particular in alkyl-thiol SAMs, where a transition from a physisorbtion in a lying geometry towards a chemisorbtion in an upright geometry has been reported [14].

However the increased coverage is normally associated with a better ordering. Although the present images do not permit a direct estimation of the coverage, the increased stability of the disorganized system for prolonged exposition points to a denser phase as compared with the organized one. This observation shows that the driving force of the assembly is to be found in molecule-substrate interactions rather than molecule–molecule interactions.

The organization obtained on Au(111) after a ~ 12-hours exposure to a suspension of PEP in tetradecane is reported in Figure 4. The image are of bad resolution, however, a SAM being observed, they reveal a better organization for this species as compared to the TPPHZ.

CONCLUSION

The self-assembling on Gold(111) of bis-bidentate ligands derived from the 1,10-phenanthroline have been studied. Like their single-bidendtate counterparts, these ligands form large edge-on alignments stabilised by the π-stacking of their large and rigid aromatic cores. An intriguing evolution towards a less ordered assembly is observed by increasing the coverage with one of the studied molecules. The presence of an idle polypyridyle function pointing upward is expected to enable further functionalization of the gold surface, e.g. through complexation.

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