Assembling Behavior of BINAP Derivative

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(Received March 11, 2002; CL-020230)

Ordered assembly of dendritic BINAP ligand has been studied by using scanning tunneling microscopy (STM). It is proposed that the molecules are arranged in a dimeric manner in the assembly.

Stereoselective synthesis of chiral organic compounds is one of the most important developments in modern chemistry over the past several decades. Many chiral transition-metal complexes are known to exhibit high activities and enantioselectivities.[1] Heterogeneous chiral catalysts are particularly attractive because it provides easy separation and recycling of the expensive catalyst after the reactions.[2] Several methodologies have been developed for the attachment of chiral catalysts to organic or inorganic solid surface via chemical bond or adsorption. In most cases, however, the immobilized chiral catalysts showed low enantioselectivity and/or reactivity as compared to the corresponding homogeneous catalyst. Unlike the homogeneous system, the heterogeneous catalysts are more complicated and the microenvironment around the active sites is usually not clear. Therefore, improved characterization should lead to better understanding of the interaction between supports and the catalytic active species, which can often help to improve the catalytic efficiency of the existing systems and develop new heterogeneous catalysts.

Scanning tunneling microscopy (STM) is one of the powerful tools in investigating molecular arrangement of organic compounds with the merits of high resolution, simple sample preparation and local information. It has been applied not only to image the structure of organic monolayers,[3–5] but also to identify molecular conformation and chirality at the submolecular level.[6,7]

2,2′-Bis(diphenylphosphino)-1,1′-binaphthyl (BINAP) (Scheme 1) is the most versatile and effective ligand among all the chiral phosphine ligands which have been studied for asymmetric catalysis.[8] Attachments of BINAP onto polymer support[9] or glass surface[10] via chemical binding or adsorption methods have also been studied. In 1999, Ohtani et al. studied the self-assembly of atropisomeric compounds on a gold surface.[11] Direct STM observation of two-dimensional chirality is obtained. In this contribution, by using STM, we have studied the assembling of BINAP derivative (Scheme 1) on highly oriented pyrolytic graphite (HOPG), which may serve as a mimic model for the heterogeneous BINAP systems.

Condensation 3,4,5-tris(*p*-decyloxyl)benzoic acid[12] with (*R*)-5,5′-diamino-BINAP at 110 °C provided the dendritic BINAP ligand in more than 80% yield (Scheme 1).[13]

The samples were dissolved in toluene (HPLC grade, Aldrich) with a concentration of less than 1%. A droplet of the solution was deposited onto a freshly cleaved surface of HOPG (quality ZYB, Digital Instruments) and dried in air prior to STM imaging.

The experiment was performed on a Nanoscope IIIa SPM (Digital Instruments, Santa Barbara, CA) at room temperature in ambient conditions. STM tips of Pt/Ir wire (90/10) were mechanically formed. All the STM images were recorded using the constant current mode of operation.

The deposition structure of BINAP molecule on graphite was simulated with the INSIGHT II program by using consistent valence force field (CVFF).[14] The conjugated gradient algorithm was used in energy minimization, with a convergence criterion set to 0.01 kcal·mol^{-1}.

Figure 1 shows a STM image obtained over a 396 × 396 Å^2 area of well-ordered assembly of dendritic BINAP ligand. In the

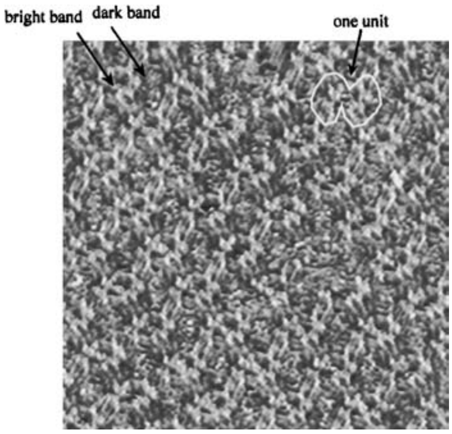
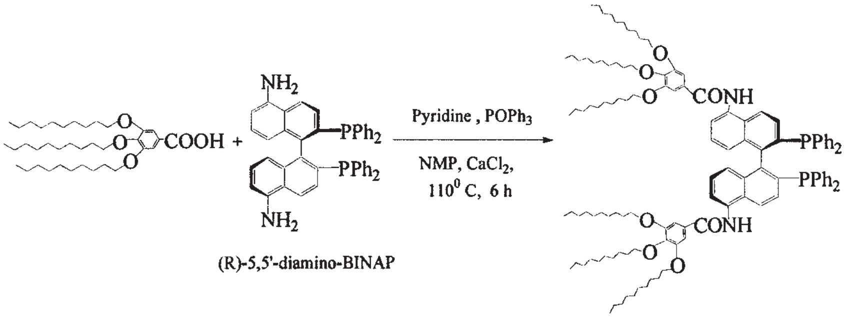


Figure 1. STM image of well-ordered assembly of dendritic BINAP ligand on a graphite surface. The white circle containing two molecules represents one unit. Tunneling condition is 1.04 nA, 856.7 mV. Scan area is 39.6 nm × 39.6 nm.



Scheme 1. Synthesis of the dendritic BINAP ligand.

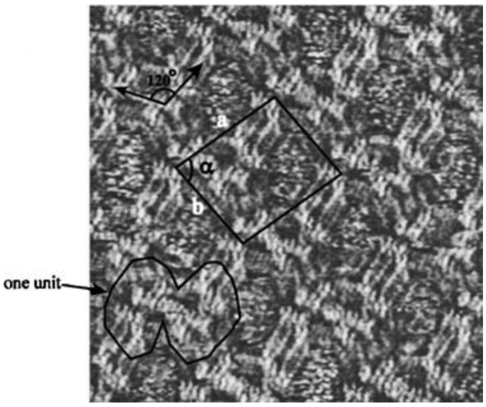


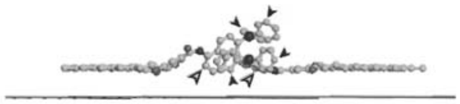
Figure 2. STM image of BINAP derivative in high resolution. The angle between two orientated alkyl chains is 120 °. The unit cell is outlined with $a = 5.7 \pm 0.1$ nm, $b = 4.8 \pm 0.2$ nm, $\alpha = 83.6 \pm 5$ °. Tunneling condition is 1.33 nA, 856.7 mV. Scan area is 18.3 nm × 18.3 nm.

image, ordered patterns are observed which indicate the packing of the molecules on the surface. It is noticed that the particular lines of butterfly-like brighter spots and darker stripe are alternating over the whole area. In the bright band, every neighboring two butterfly-like structures form one unit. The high-resolution image of BINAP derivative is presented in Figure 2. In one unit, some round dots are recognizable. Four to six spots in one butterfly-like molecule can be clearly observed, which shows part of aromatic rings flatten down on the HOPG surface. Surrounding the bright spots, two orientated alkyl chains with the angle about 120 ° are discernible. The length of alkyl chains is measured to be 1.3 ± 0.1 nm, which is commensurate with the length of a decane molecule in its all-trans conformation. The formation of dimer may be attributed to the interaction of Π-Π stack among phenyl groups. Using the lattice structure of the underlying graphite as an internal calibration, we determined the dimension and orientation of the repeating unit. A unit cell with $a = 5.7 \pm 0.1$ nm, $b = 4.8 \pm 0.2$ nm, $\alpha = 83.6 \pm 5$ ° is outlined in Figure 2.

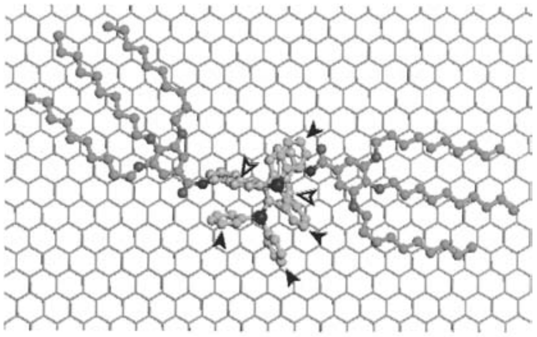
Figure 3 is the simulation result of the adsorbed molecule on HOPG surface. Due to the strong interaction between substrate and alkyl substitutions, all the six flexible chains are parallel to the surface of HOPG in all-trans conformation (Figure 3b). It has been reported that the two phenyl groups of phosphine are perpendicular to each other, and only part of binaphthalene and one of the phenyl rings connected with phosphor are co-planar.[15] On the surface, considering the interaction between the phenyl groups and HOPG, the whole arrangement of BINAP part is distorted to some extent. Most of the phenyl groups tend to be close to the substrate and pack more densely (Figure 3a). One phenyl group and part of naphthalene are overlapping (Figure 3b). The superposition is one of the reasons that all the spots in the image do not have the same contrast. According to the image, one of the most possible models is proposed (Figure 4), which agrees with the image quite well.

In summary, on a graphite surface, we studied the structure of BINAP derivative by STM. Ordered patterns were observed and the fine structure was investigated, which is fitted with the simulation result.

The authors thank the National Natural Science Foundation (No. 20103008) and the Foundation of the Chinese Academy of Sciences for financial support.



(a) side view



(b) top view

Figure 3. Energy-minimized structure of BINAP derivative. In BINAP part, the phenyl groups are indicated by solid arrowheads, while the naphthalene groups are indicated by hollow arrowheads. The two big balls among the phenyl groups represent phosphor atoms.

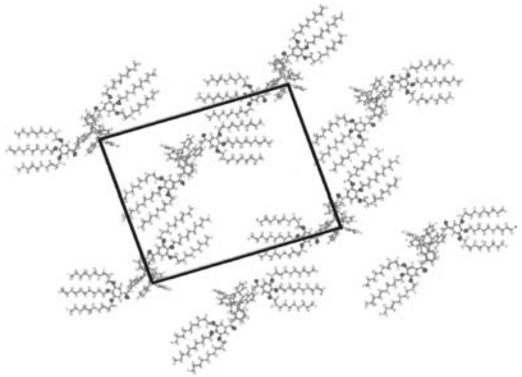


Figure 4. Packing model of BINAP ligand with the energy-minimized structure.

References and Notes

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