

## The Fluorescence Study of the Induced Adsorption Orientation of Biphenyl Derivatives on Au Colloidal Surface

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Self assembled monolayers (SAMs) are surfaces on which a single layer of molecules is formed when a solution of the desired molecule is dropped onto the substrate surface. A common example for SAMs is an alkanethiol on gold which forms an ordered assembly with the alkyl chains packing together due to van der Waals forces. A variety of studies were performed on the alkanethiol on metal surfaces due to the simplicity to simulate a model system. However, alkanethiols are not adequate for the densely packed and well-ordered self assembled monolayers (SAMs) due to the island formation and kink conformation.<sup>1,2</sup>

In many cases, applications require more stable surfaces, and so designed SAMs surfaces were suggested in studies of molecular recognition, bimaterial interfaces, cell growth, crystallization, and many other systems.<sup>3</sup> Aromaticthiol SAMs on gold received attention due to not only their rigidity and stability but also high electronic conductivity and nonlinear optical properties.<sup>4</sup> These properties of aromaticthiol SAMs are affected by various interactions such as the sulfur head group-substrate interaction, the interchain van der Waals interaction, and interchain end group interactions. Since the biphenyl groups have  $\pi$  electrons around the phenyl rings, they may form a rigid and stable SAMs through the strong van der Waals interactions.

Although biphenyl derivatives are useful for SAMs, the molecules which can have a perpendicular orientation at a surface will be more useful for this purpose. For example, Liu *et al.* studied adhesion, friction, and wear properties of biphenyl thiol self-assembled monolayers of which orientation is perpendicular to the surface.<sup>5</sup> SAMs of 4-biphenylthiol (BT) formed on polycrystalline silver substrates were characterized by Weckenmann *et al.* and were revealed to be oriented perpendicular to the surface.<sup>6</sup>

However, there are many biphenyl derivatives that do not form a densely packed and well-ordered SAMs because of a flat orientation. The biphenyls with -CN, -NH<sub>2</sub>, and -COOH functional groups adsorbed on Au colloidal surface are classified into this category.<sup>7</sup> Thus it is of our curiosity to know whether the adsorption orientation will be modified with the help of a supporting material such as cyclodextrins (CDs).

The usage of CDs will be suitable for this purpose, since it will contain biphenyls in its cavity through van der Waals interaction,<sup>8</sup> while the hydroxyl groups of CDs will be adsorbed perpendicularly onto the metal surface through non-bonding electrons of oxygen atoms consisting of hydroxyl groups.<sup>9</sup> In this case the molecules inside the cavity will take the perpen-

dicular form, and its orientation will be very useful for the molecular engineering of the surface.

### Experiment

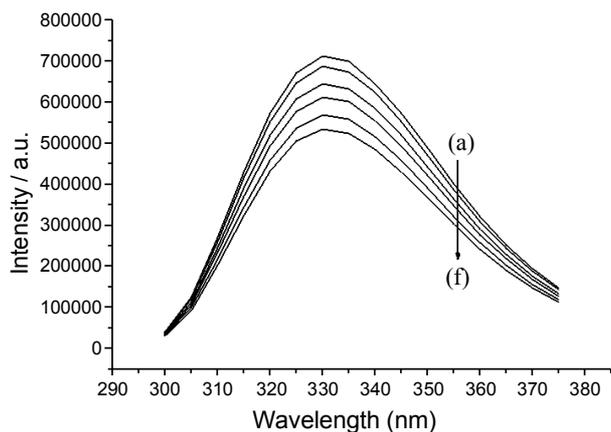
4-Biphenylcarboxylic acid (BPCA), 4-cyanobiphenyl (CNBP), 4-aminobiphenyl (AMBIP), 4-biphenylacetonitrile (BPAN), and  $\alpha$ -cyclodextrin ( $\alpha$ -CD) were all purchased from Sigma-Aldrich Inc. and used as received. Dimethylformaldehyde (DMF) is of spectrophotometric grade from Sigma-Aldrich Inc. and used to dissolve the samples in a ratio of 30% (v/v) in water. The concentration range was 10<sup>-6</sup> M for all the molecules, and 10<sup>-5</sup>-10<sup>-6</sup> M for  $\alpha$ -CD. This concentration is low enough to prevent the dimerization for the molecules under study. The procedure for the preparation of Au colloid is described elsewhere,<sup>10,11</sup> and the concentration was calculated to be 10<sup>-5</sup> M.

The fluorescence spectra were recorded on a PTI time-master 200. All the spectra were obtained after accumulating 10 scans with stepsize of 2 nm. The fluorescence intensity was compared before and after the addition of  $\alpha$ -CD to either the bare or adsorbed molecules on Au surface.

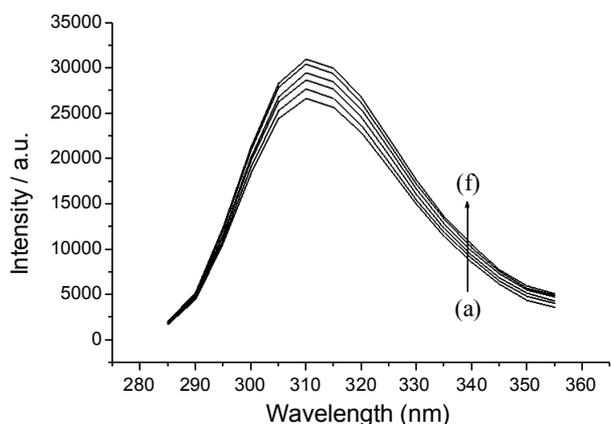
### Results and Discussion

**Interaction with  $\alpha$ -CD.**  $\alpha$ -CD consisting of six glucose residues has lipophilic cavity with inner diameter of 4.7-5.3 Å, and forms inclusion complexes with various kinds of compounds.<sup>12,13</sup> It is well known that the hydrophobic moiety like biphenyl group tends to protrude into the cavity of  $\alpha$ -CD in aqueous solution. This phenomenon is due to the hydrophobic interactions between the cavity of  $\alpha$ -CD and the hydrophobic moiety. Therefore, most studies for the aromatic groups show the similar results though the formation constant is different from the molecule by molecule. In order to study the interaction with  $\alpha$ -CD, several biphenyl derivatives with different functional groups such as CNBP, BPCA, and AMBIP were selected, and the change in fluorescence intensity was monitored while adding  $\alpha$ -CD. The selected molecules did not follow the usual trend. As the concentration of  $\alpha$ -CD increased the intensity of the fluorescence decreased as can be seen in Figure 1; Only the CNBP is shown here, but the other two molecules showed the same trend. Considering that most biphenyl derivatives are reported to be included in the cavity of  $\alpha$ -CD, this result is very unusual.

Hydrogen bonding was reported to quench the fluorescence



**Figure 1.** Fluorescence spectra of CNBP ( $1.0 \times 10^{-6}$  M) as a function of  $\alpha$ -CD. Arrow indicates the change in fluorescence intensity with increasing concentration: (a) 0 mM, (b) 3 mM, (c) 6 mM, (d) 9 mM, (e) 12 mM, (f) 15 mM.

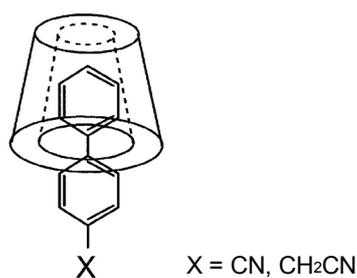


**Figure 2.** Fluorescence spectra of BPAN ( $1.0 \times 10^{-6}$  M) as a function of  $\alpha$ -CD. Arrow indicates the change in fluorescence intensity with increasing concentration: (a) 0 mM, (b) 3 mM, (c) 6 mM, (d) 9 mM, (e) 12 mM, (f) 15 mM.

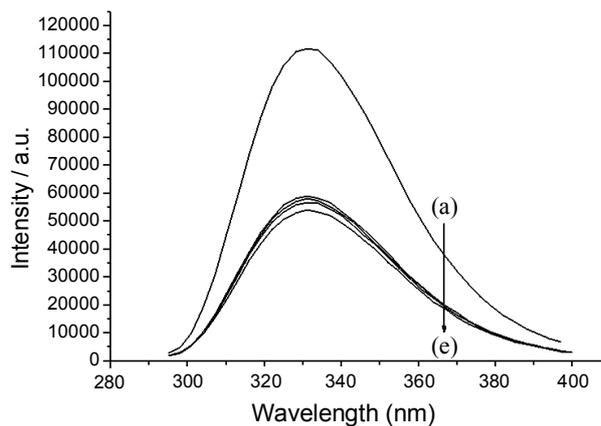
in a host-guest complex.<sup>14,15</sup> The functional groups such as -CN, -COOH, and -NH<sub>2</sub> have large enough dipole moment for hydrogen bonding. Therefore, a hydrogen bonding may have influenced the quenching of the fluorescence. For these molecules, any type of hydrogen bonding will quench the fluorescence because of good conjugation between the biphenyl moiety and the functional groups.

This suggestion is evidenced by examining a similar molecule, BPAN. For this molecule, the conjugation is blocked by a methylene group existing between biphenyl moiety and cyano group. Therefore, although any type of hydrogen bonding is formed fluorescence intensity will be increased as long as the biphenyl moiety is embedded in a cavity of  $\alpha$ -CD. This result is shown in Figure 2. Based on the fluorescence study for biphenyl derivatives, the plausible complex form with  $\alpha$ -CD can be shown in Figure 3.

**Adsorption on Au colloidal surface.** The monitoring of the fluorescence intensity with respect to the concentration of Au colloid provides the information about whether the molecules are adsorbed or not on the Au colloidal surface. It is well known that the fluorescence intensity is quenched when the molecules are adsorbed on the metal surfaces. This fact enables



**Figure 3.** The inclusion complex of biphenyl derivatives with  $\alpha$ -CD.

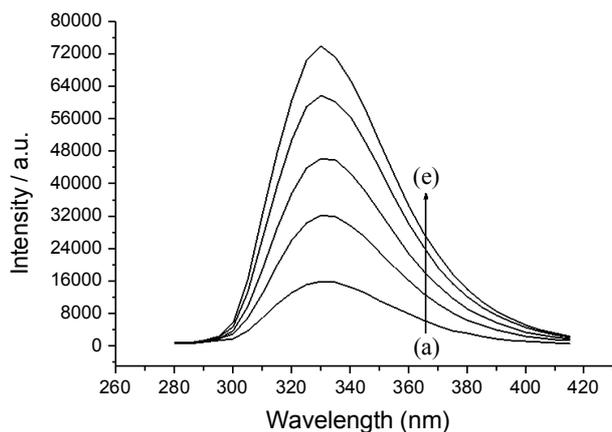


**Figure 4.** Fluorescence spectra of CNBP ( $1.0 \times 10^{-6}$  M) as a function of Au colloid. Arrow indicates the change in fluorescence intensity with increasing concentration: (a) 0 mM, (b)  $1.0 \times 10^{-7}$  mM, (c)  $1.0 \times 10^{-6}$  mM, (d)  $1.0 \times 10^{-5}$  mM, (e)  $1.0 \times 10^{-4}$  mM, (f)  $1.0 \times 10^{-3}$  mM.

the Raman spectroscopy to obtain the vibrational spectra from the fluorescent molecules by suppressing fluorescence. Surface enhanced Raman spectroscopy (SERS) is the method widely used for the fluorescent molecules that were not susceptible to the conventional Raman spectroscopy.

The fluorescence intensity was decreased with addition of Au colloid as can be seen in Figure 4. This was applied to all the molecules under present study. The decrease in fluorescence intensity indicates that the molecules are adsorbed on the metal surfaces unless a collisional quenching is dominant. The adsorption orientations of the molecules on Au colloidal surfaces were well studied for various molecules by SERS. The orientation of BPAN was studied with SERS by monitoring the biphenyl moiety and carboxylate groups on Au colloidal surface. The result showed that the BPAN was adsorbed with flat orientation with respect to the surface. This is evidenced by the characteristic Raman bands for benzene and carboxylate groups.<sup>16</sup> We studied 4'-cyanobiphenyl-4-carboxylic acid to elucidate the adsorption orientation by SERS and found that the CN group was adsorbed through  $\pi$  electrons on Au surface.<sup>7</sup> This was evidenced by the red shift of the CN stretching mode by  $7 \text{ cm}^{-1}$  compared to the normal band. The mechanism for the flat adsorption of CN is due to the  $\pi$  electrons of CN. The AMBP was also revealed to be adsorbed with a flat orientation. Judging from the above facts, we consider the molecules of our interest to be adsorbed on the Au colloidal surface with flat orientation.

**Intercalation of adsorbates into  $\alpha$ -CD.** It is valuable to know the interaction between  $\alpha$ -CD and Au colloidal surface

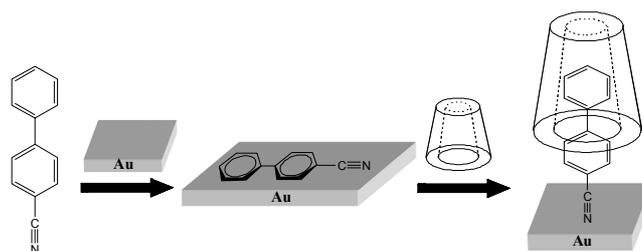


**Figure 5.** Fluorescence spectra of CNBP ( $1.0 \times 10^{-6}$  M) - Au ( $1.0 \times 10^{-5}$  M) complex as a function of  $\alpha$ -CD. Arrow indicates the change in fluorescence intensity with increasing concentration: (a) 0 mM, (b) 5 mM, (c) 10 mM, (d) 15 mM, (e) 20 mM.

from the view point of orientation. The interaction between Au nanoparticle and  $\beta$ -CD was studied by Huang *et al.*<sup>17</sup> They found that the interaction between Au nanoparticle and  $\beta$ -CD is attributed to the chemisorption via hydroxyl group. Liu *et al.*<sup>18</sup> also studied the interaction between them, and found that the physisorption is involved. The size of one Au colloidal particle in our experiment is about 10 nm, and is too big to fit into the cavity, so the hydroxyl groups are able to adsorb on the Au surface *via* either chemisorption or physisorption. In this case, the orientation of  $\alpha$ -CD adsorbed on the Au surface is more likely perpendicular. Accordingly, the orientation of the molecule in the cavity would have the same as that of  $\alpha$ -CD, resulting in a perpendicular orientation. However, the cavity size of  $\alpha$ -CD is not big enough for the biphenyl moiety to pass through it. As a result, there will be no interaction between the hydroxyl group and the metal surface because only the capping of  $\alpha$ -CD will occur to the molecule, which is adsorbed strongly on the metal surface.

The fluorescence intensity was increased with the addition of  $\alpha$ -CD as can be seen in Figure 5. The spectral feature for the adsorbates on Au colloid is quite opposite to that of bare molecule when the concentration of  $\alpha$ -CD was increased. The reason for the enhancement of the fluorescence was due to the intercalation of molecules into the hydrophobic cavity. When the molecule is adsorbed on Au particle, there is no functional group that can form hydrogen bonding with hydroxyl group of the rim. And thus, no quenching occurs through hydrogen bonding with  $\alpha$ -CD. It is much easier for the molecules to protrude into cavity of  $\alpha$ -CD, now. In this case, the fluorescence quenching occurs due to both Au colloid and solvent, mainly water. If the molecules are intercalated into the cavity, the quenching by water should be protected. This is the case for our present system. The increase in fluorescence intensity with the addition of  $\alpha$ -CD manifests the intercalation of the molecule into the cavity.

It is not readily understandable that the molecules adsorbed with flat orientation protrude into the cavity. The diameter of the cavity is 4.7-5.3 Å for  $\alpha$ -CD, while the bond length of the biphenyl itself is about 7 Å.<sup>19</sup> Therefore, the encapsulation of the molecules by  $\alpha$ -CD is impossible with a flat orientation. In



**Figure 6.** The schematic diagram for the change in adsorption orientation of BPCN with  $\alpha$ -CD.

order for the molecules to protrude into the cavity, the orientation of the molecules should be tilted or perpendicular to Au colloidal surface. Thus, the resultant enhancement of the fluorescence could be explained only by the intercalation with a tilted or perpendicular orientation. Considering the dimension of the cavity of  $\alpha$ -CD, the biphenyl moiety would not penetrate  $\alpha$ -CD. Accordingly, the possible structure of the complex would be the capping of  $\alpha$ -CD without adsorption of the hydroxyl group. The hypothesis obtained by fluorescence spectroscopy will be more clarified by the Raman and AFM studies. The SERS at the appropriate positions as indicated by AFM image will be the evidence for our suggestion. NMR study will also give the idea about the intercalation because the downfield of the hydrogens inside the cavity of  $\alpha$ -CD would be expected. This is a subject of our further investigation.

The mechanism for the induced orientation is illustrated in Figure 6. The molecules are adsorbed with a flat orientation on Au colloidal surface, at first. As the  $\alpha$ -CD was added to the molecules on the Au surface, the orientation changed to tilted or perpendicular so that the intercalation of the molecules may occur.

## Conclusion

We have tried to change the adsorption orientation of the biphenyl derivatives on the Au colloidal surfaces with  $\alpha$ -CD. For this purpose, the molecules adsorbed with a flat orientation on Au colloidal surfaces, such as BPCA, BPCN, BPAN were selected and then  $\alpha$ -CD was added. From the increase of the fluorescence intensity with the addition of  $\alpha$ -CD, the intercalation of the molecules into the hydrophobic cavity was inferred. This fact suggests that the adsorption orientation was changed from flat to tilted or perpendicular orientation. All the judgement was made with the help of the fluorescence spectroscopy with the concentration as low as  $10^{-6}$  M. The induced adsorption may be used to modify the SAMs through the molecular engineering such as covalent immobilization for medical and bioanalytical application.

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