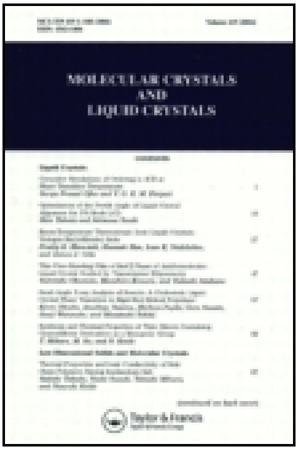

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We synthesized 25,26,27,28-tetrakis(mercaptobuthoxy)-5,11,17,23-[2,2′-thioxy(o-phenylene)thioxy-piperidino]calix[4]arene **[1]**, *25,26,27,28-tetrakis(mercaptobuthoxy)-5,11,17,23-[2,2′-thioxy(o-phenylene)thioxy-amino]calix[4]arene* **[2]** *and 25,26,27,28-tetrakis(mercaptobuthoxy)-5,11,17,23-[2,2′-thioxy(o-phenylene)thioxy-aminopyrene] calix[4]arene* **[3]** *containing four alkyl thiol linkages, which allow the calix[4] arene to attach on the gold surface. We observed the binding of calix[4]arene derivatives and aromatic molecules with surface plasmon resonance and confirmed complexation of aromatic nitriles on calix[4]arene derivatives with FT-IR peak.*

Keywords: calix[4]arene; self-assembled monolayer; surface plasmon resonance

INTRODUCTION

Since the birth of calix[4]arene in the 1870's, the use of these molecules for chemical separations was consistently challenged [1–4]. The balance between flexibility and rigidity of calix[4]arene derivatives facilitates the complex formation with organic molecules. It is rather difficult to have specificity toward organic molecules with complexity and diversity. Recent investigation and development of sensors for volatile organic compounds(VOC) require high sensitivity and

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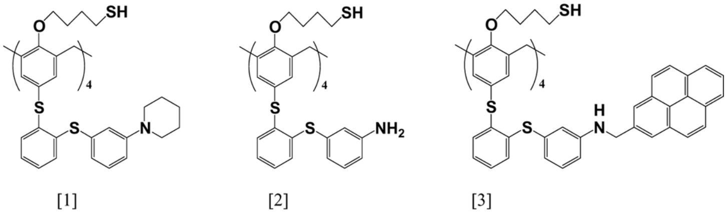
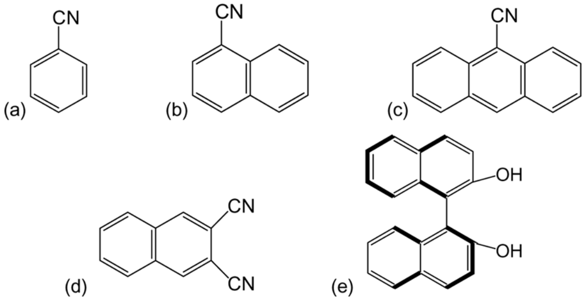


SCHEME 1 The molecular structures of 25,26,27,28-tetrakis(mercaptobuthoxy)-5,11,17,23-[2,2′-thioxy(o-phenylene)thioxy-piperidino]calix[4]arene (TMTPTP) **[1]**, 25,26,27,28-tetrakis(mercaptobuthoxy)-5,11,17,23-[2,2′-thioxy (o-phenylene)thioxy-amino]calix[4]arene (TMTPTA) **[2]** and 25,26,27,28-tetrakis(mercaptobuthoxy)-5,11,17,23-[2,2′-thioxy(o-phenylene)thioxy-aminopyrene] calix[4]arene (TMTPTAP) **[3]**.

selectivity. The semi-rigidity of calix[4]arene bucket and the flexibility are endowed from alkyl thiols and aryl sulfide. In this study we synthesized **[1]**, **[2]**, and **[3]** with four alkyl thiol linkages, which allow the calix[4]arene to attach on the gold surface. With the surface plasmon resonance (SPR) spectroscopy [5], binding of calix[4]arene derivatives to the gold surface and binding of aromatic molecules with nitrile substituent to the calix[4]arene derivatives were monitored.

EXPERIMENTAL

The synthesis of **1**, **2**, and **3** has been reported elsewhere [6–8]. The calix[4]arene derivatives were dissolved in chloroform to generate self-assembled monolayer on gold substrates. The gold substrate was



SCHEME 2 The organic materials of benzonitrile **(a)**, 1-naphthonitrile **(b)**, 9-cyanoanthracene **(c)**, 2,3-dicyanonaphthalene **(d)**, and (s)-(-)-1,1′-bi-2-naphthol **(e)**.

made by deposition with 48 nm thickness onto chrome (2 nm) which is the bottom layer on microscope cover glass. The gold substrate was washed with piranha solution for 30 min followed by washing with ethanol and water twice each. The gold substrate was dipped in chloroform solutions which contained calix[4]arene derivatives for 24 hours and washed with chloroform. The complex formation of calix[4]arene with organonitriles were followed. The dipping in each chloroform which had each organic material. The dipping period was 24 hours and the physically adsorbed organic molecules were washed with fresh chloroform. The organonitriles used in this study are benzonitrile, 1-naphthonitrile, 9-cyanoanthrcene, 2,3-dicyanonaphthalene and (s)-(-)-1,1′-bi-2-naphthol.

The surface plasmon resonance spectra was obtained from the home-made set-up, which contained the He-Ne laser (20 mW, Lacos, lasertechnik, GmbH, SNA7470A2), a goniometer (Suruga Seiki, Model D80, terminal D700) and optical multimeter (Ando Aq2150). The software to control goniometer and the receiving optical data was programmed in our laboratory. We confirmed nitriles with FT-IR (Nicolet, MAGNA-IR 560 SPECTROMETER).

RESULTS AND DISCUSSION

The calix[4]arene derivatives, **1**, **2**, and **3** were attached on bare gold, the SPR absorption angle changed from 44.08° for bare gold to 44.16° for **1**, to 44.28° for and to 44.48° for **3** (Fig. 1). The organonitriles were readily adsorbed on the **1**, **2**, and **3** attached on gold substrate. The complexation was accomplished in 30 min.

Since the pyrene moiety on **3** is larger than the other amines, the SPR angle for **3** shows pronounced shift from bare gold. Among the organonitriles studied, 9-cyanoanthrcene and 2,3-dicyanonaphthalene exhibits more pronounced SPR angle shift. The higher affinity of 9-cyanoanthrcene and 2,3-dicyanonaphthalene to the calix[4]arene monolayers can be explained by size, dipole-dipole interaction and specific molecular interactions between host and guest molecules [9], such as charge transfer complexes and hydrogen bonding interactions. The organonitriles have similar dipole moment, except 2,3-dicyanonaphthalene. The dipole moments of organonitriles used in this study are 3.3 D (benzonitrile), 3.4 D (1-naphthonitrile), 3.5 D (9-cyanoanthracene), 6.3 D (2,3-dicyanonaphthalene) and 2.4 D ((s)-(-)-1,1′-Bi-2-naphthol). The dimensions of organonitriles (long axis; short axis) are 6.6 Å; 4.4 Å (benzonitrile), 6.8 Å; 6.6 Å (1-naphthonitrile), 9.3 Å; 6.6 Å (9-cyanoanthracene), 8.2 Å; 5.2 Å (2,3-dicyanonaphthalene) and

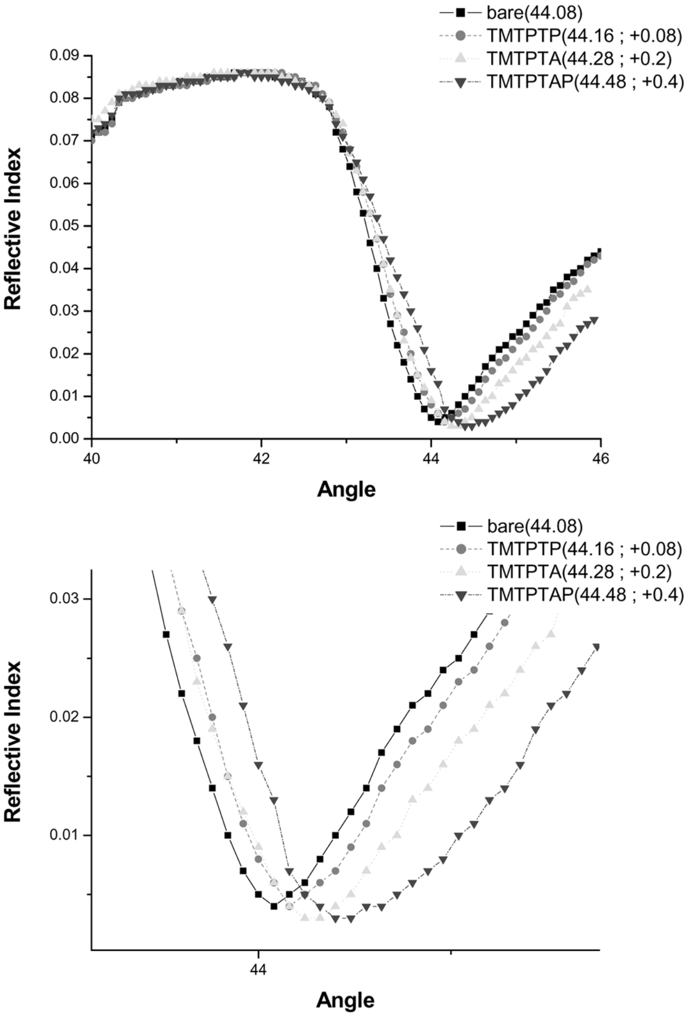


FIGURE 1 The surface plasmon resonance absorption spectra of **1**, **2**, and **3** for 24 hours.

7.0 Å; 8.5 Å ((s)-(-)-1,1′-bi-2-naphthol), which were calculated with MOPAC. Since the organonitriles do not have strong hydrogen bonding, capability of forming charge transfer complex and size effect are synergetically attributed to the comlexation of organonitriles to the calix[4]arene attached on gold substrates.

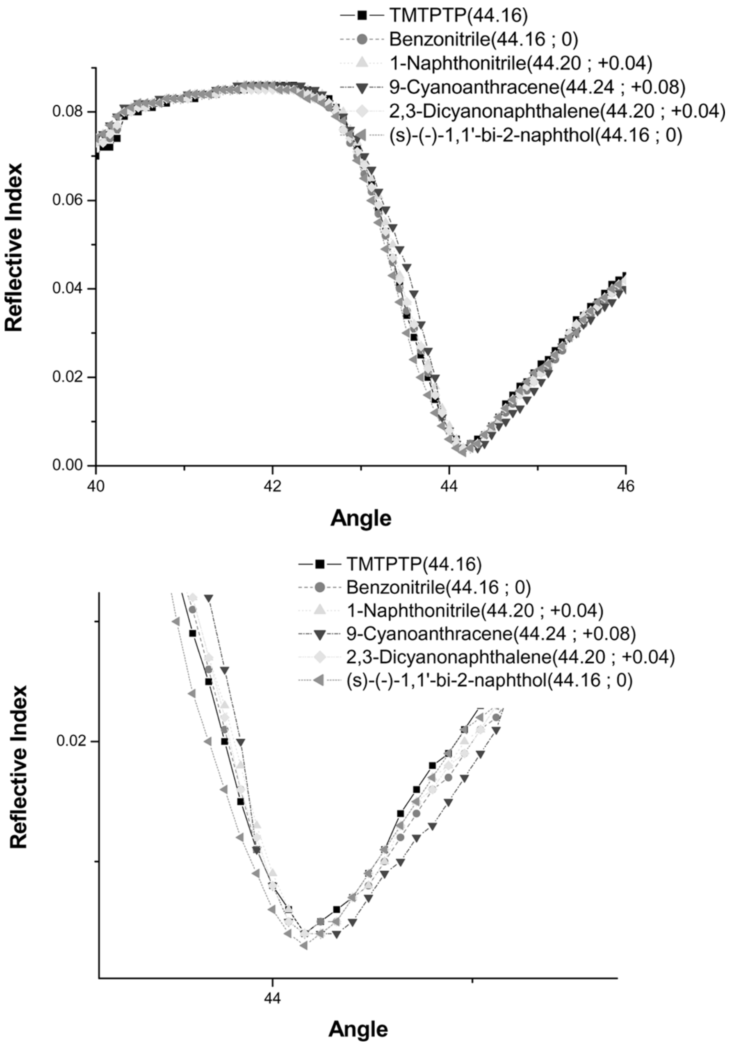


FIGURE 2 The surface plasmon resonance absorption spectra of **1** and benzonitrile, 1-naphthonitrile, 9-cyanoanthracene, 2,3-dicyanonaphthalene and (s)-(-)-1,1′-bi-2-naphthol, adsorbed on **1** attached on gold substrate.

It is interesting to observe the binding of benzonitrile only occurs slightly on the monolayer of **3** (Figs. 2, 3, and 4) and 1-naphthonitrile have little affinity to calix[4]arene derivatives attached on gold substrate. These results indicate that the small size molecules do not have strong binding affinity to the calix[4]arene derivatives on gold. Strong

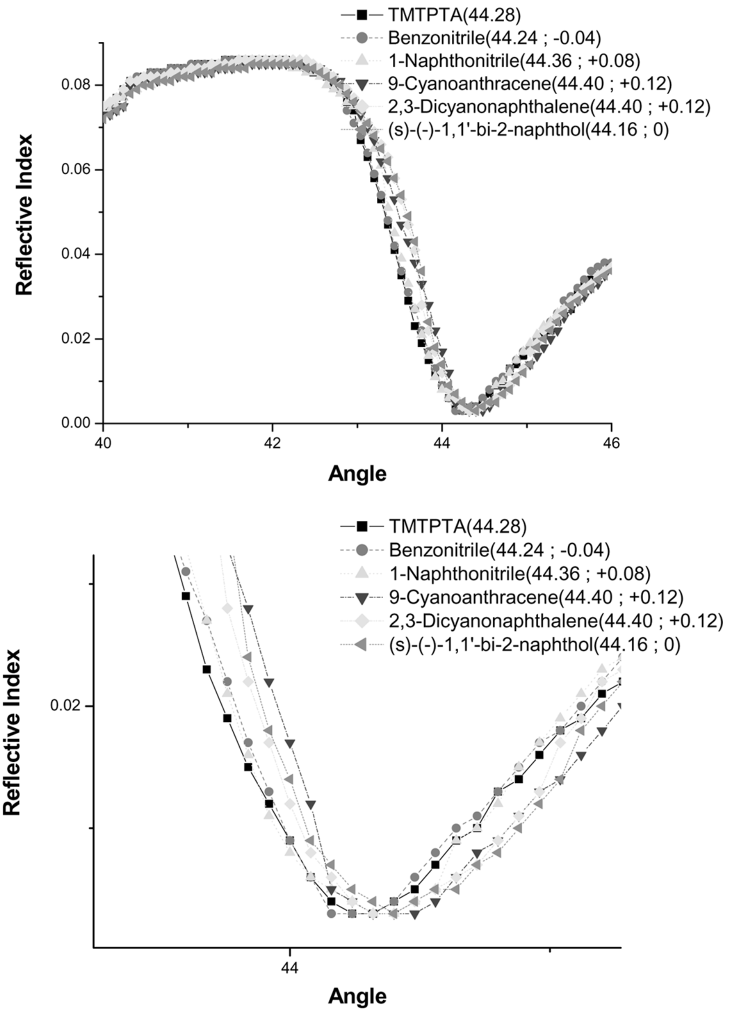


FIGURE 3 The surface plasmon resonance absorption spectra of **2** and benzonitrile, 1-naphthnitrile, 9-cyanoanthracene, 2,3-dicyanonaphthalene and (s)-(-)-1,1′-bi-2-naphthol, adsorbed on attached on **2** gold substrate.

interactions of 9-cyanoanthracene and 2,3-dicyanonaphthalene strongly suggest that the charge transfer complex formation and the size fitting between host and guest molecules work synergetically to bind organonitriles. The binding of organonitriles on monolayer of **3** attached on gold substrate was confirmed with $-$CN stretching band at 2270 cm^{-1} (Fig. 5). The size of (s)-(-)-1,1′-bi-2-naphthol is bigger than

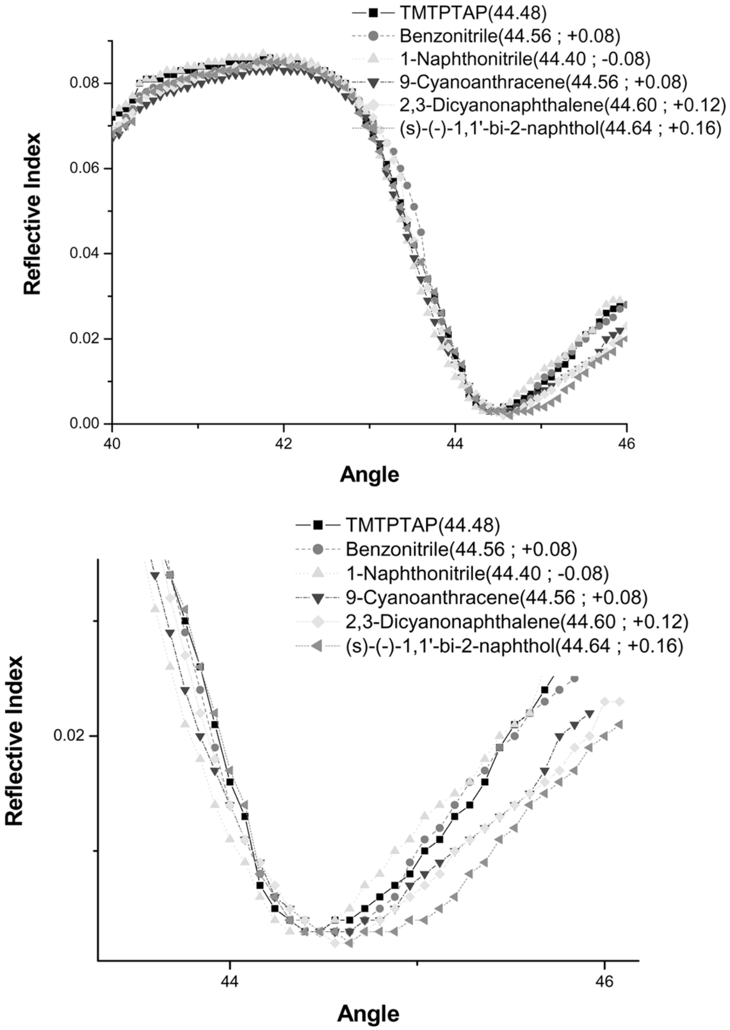


FIGURE 4 The surface plasmon resonance absorption spectra of **3** and benzonitrile, 1-naphthnitrile, 9-cyanoanthracene, 2,3-dicyanonaphthalene and (s)-(-)-1,1′-bi-2-naphthol, adsorbed on **3** attached on gold substrate.

the flat organonitriles and it does not have an electron withdrawing group to form a charge transfer complex. Specific binding occurs only on **3** on gold substrate. This is only due to the bigger cavity generated with pyrene units of **3**.

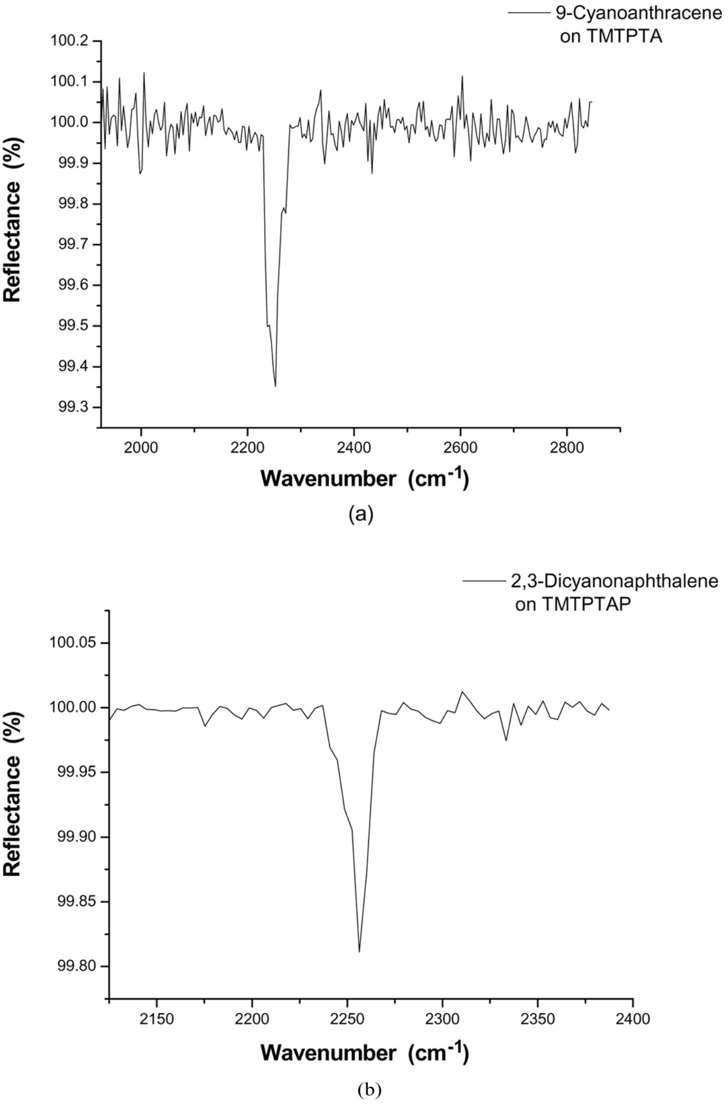


FIGURE 5 The FT-IR reflectance spectra of 9-cyanoanthracene (a) and 2,3-dicyanonaphthalene (b) on the monolayer of **3**.

CONCLUSIONS

The SPR studies strongly indicate that the calix[4]arene derivatives **1**, **2**, and **3** bind on the gold substrates. Calix[4]arene containing aryl sulfide and amine moieties are important for the binding of organonitriles.

REFERENCES

[1] Baeyer, A. (1872). *Ber.*, *5*, (25), 280, 1094.
[2] Niederl, J. B. & Vogel, H. J. (1940). *J. Am. Chem. Soc.*, *62*, 2512.
[3] Böhmer, V., Chhim, P., & Kämmerer, H. (1979). *Makromol. Chem.*, *180*, 2503.
[4] Lumetta, G. J., Rogers, R. D., & Gopalan, A. S. (2000). *American Chemical Society Washington*, DC, ACS SYMPOSIUM SERIES 757, Calixarenes for Separation.
[5] Knoll, W. (1998). *Annu. Rev. Phys. Chem.*, *49*, 569.
[6] Yoon, K. & Kim, K. (2005). *J. Org. Chem.*, *70*(2), 427.
[7] Yoon, K. & Kim, K. (2005). *J. Org. Chem.*, *70*(14), 5741.
[8] Yoon, K. & Kim, K. *ARKIVOC* 2003 (*ixxx*), 138.
[9] Kunsági-Máté, S., Nagy, G., & Kollár, L. (2001). *Analytica Chimica Acta*, *428*, 301.