

## Conductivity Comparison of Calix[8]arene-MWCNTs Through Spin Coating Technique

(Perbandingan Kekonduksian Kaliks[8]arena-MWCNTs Melalui Teknik Penglitupan Putaran)

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### ABSTRACT

*In this study, we investigated the conductivity enhancement of calix[8]arene-multi-walled CNTs (MWCNTs) thin film. Two types of calix[8]arenes were used, which were 5,11,17,23,29,35,41,47-p-tert-butyl-49,50,51,52,53,54,55,56-oktakis[(carboxy)-pentoxy] -calix[8]arene (C[8]1) and 49,50,51,52,53,54,55,56 -octahydroxycalix[8]arene (C[8]2). The monolayer properties of these two types of calix[8]arene on water subphase were examined. Later, the thin films were fabricated by combining different ratios of each types of calix[8]arene with MWCNTs using spin coating deposition technique. Then, the developed thin films were characterized using surface potential meter and four point probe. Thin films of C[8]2 with hydroxyl groups at lower rims demonstrated higher surface potential and conductivity as compared to the thin films of C[8]1 with upper rims of tert-butyl groups and lower rims of carboxyl groups. These results indicated that the conductivity of calixarene thin films can be enhanced by MWCNTs through simple spin coating technique.*

*Keywords: Calixarene; conductivity; spin coating deposition; surface potential; surface pressure*

### ABSTRAK

*Dalam kajian ini, kami mengkaji tentang peningkatan kekonduksian lapisan nipis kaliks[8]arena-nanotub karbon multi-dinding (MWCNTs). Dua jenis kaliksarena digunakan, iaitu 5,11,17,23,29,35,41,47-p-tert-butyl-49,50,51,52,53,54,55,56-oktakis[(karboksi)-pentoksi] -kaliks[8]arene (C[8]1) dan 49,50,51,52,53,54,55,56-oktahidroksikaliks[8]arene (C[8]2). Sifat lapisan mono kaliksarena atas permukaan air telah dikaji. Kemudian, lapisan nipis telah dibentuk dengan menggunakan nisbah yang berbeza bagi setiap jenis kaliks[8]arene dengan MWCNTs menggunakan teknik penglitupan putaran. Seterusnya, lapisan nipis tersebut dicirikan dengan menggunakan meter potensi permukaan dan empat penduga titik. Lapisan nipis C[8]2 dengan kumpulan hidrosil pada rim bawah menunjukkan potensi permukaan dan kekonduksian yang lebih tinggi berbanding dengan lapisan nipis C[8]1 dengan rim atas yang terdiri daripada kumpulan tert-butyl dan rim bawah yang terdiri daripada kumpulan karboksil. Keputusan ini menunjukkan bahawa kekonduksian lapisan nipis kaliksarena boleh dipertingkatkan dengan MWCNTs melalui teknik penglitupan putaran yang ringkas.*

*Kata kunci: Kaliksarena; kekonduksian; penglitupan putaran; potensi permukaan; tekanan permukaan*

### INTRODUCTION

Among all the supramolecules used to form sensors, calixarene stood out as one of the promising candidates due to host-guest properties that can be modified through alteration of upper and lower rims, resulting in different conformations of calixarenes (Botha et al. 2014; Csokai et al. 2006). These conformations have high selective binding properties toward certain ionic or molecular substance (Chen et al. 2000; Yang et al. 2015) while some even showed chromogenic sensing properties (Bingol et al. 2010; Tabakci & Yilmaz 2014).

Calix[8]arene have been previously fabricated into Langmuir-Blodgett (LB) thin film and exposed to volatile organic solvents (chloroform, benzene, toluene and ethyl alcohol) as reported by Çapan et al. (2010). From the study, the LB film gave fast and reversible sensing response to chloroform. Similar report about the capability of calix[8]arene as sensing molecule also stated in Qureshi et al. (2008). The binding ability and extraction

efficiency of calix[8]arene with transition metals is investigated. Despite its superior sensing property, these supramolecules have poor conductivity (Chaâbane et al. 1994).

On the other hand, carbon nanotubes (CNTs) are considered as a superior conductor. CNTs can detect strong charge transfer interaction in the host-guest binding of supramolecules and cause a change in their conductance, result in a more sensitive sensor (Zhu & Fang 2014). Several previous studies such as Gaichore and Srivastava (2012), Mermer et al. (2012) and Wang et al. (2012), demonstrated that the developed sensors have synergistic effect after combined the calixarene and CNTs together, lead to the production of better result in the guest detection. Besides the addition of CNTs to enhance the sensing property of calixarene, other approach included the addition of conducting polymer (Gokoglan 2015; Vigalok & Swager 2002). However, this required the synthesis of the polymer first before composite with calixarene.

In this work, the multi-walled CNTs (MWCNTs) were integrated with calix[8]arenes. The aim was to increase the conductivity property of calix[8]arene as to synthesize composite that could be a better conductive film for the supramolecular electronic sensor. The resulting material should have retained the excellent properties from both that give rise to the needed good electroanalysis signal later in term of sensing. Different combination ratios of calix[8]arenes and MWCNTs were employed in this work to study the optimum ratio between calix[8]arene and CNTs for future research.

## MATERIALS AND METHODS

### MATERIALS

Two types of calix[8]arenes were selected as the core molecules in this research. 5,11,17,23,29,35,41,47-p-tert-butyl-49,50,51,52,53,54,55,56-oktakis[(carboxy)-pentoxy]-calix[8]arene (C[8]1) was generously contributed by Dr. Mary Deasy's research group, Institute of Technology Tallaght, Dublin, Ireland while 49,50,51,52,53,54,55,56-octahydroxycalix[8]arene (C[8]2) was purchased from Sigma Aldrich. The structure of both calix[8]arenes are shown in Figure 1. The C[8]1 consists of carboxyl groups at the lower rims and upper rims of tert-butyl groups whilst C[8]2 has hydroxyl groups positioned at lower rims.

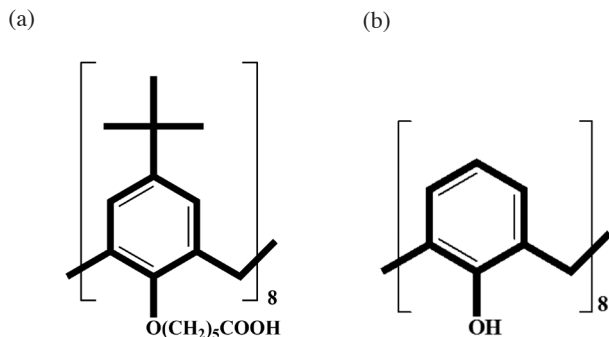


FIGURE 1. Chemical structure of (a) C[8]1 and (b) C[8]2

MWCNTs with diameter range from 10 - 20 nm, length  $>1 \mu\text{m}$  and purity  $>95\%$  were purchased from Shenzhen Nanotech, China. Chloroform ( $\text{CHCl}_3$ ,  $>99.8\%$  purity, Fisher Scientific) was used as a solvent to dissolve the calix[8]arenes. No further purification process required for all the reagents. Two types of substrate ( $25 \text{ mm} \times 25 \text{ mm}$ ) were used - silicon (Si) substrate for surface potential analysis and indium tin oxide (ITO) coated glass substrate for conductivity analysis.

### SAMPLE PREPARATIONS

For each type of calix[8]arene/MWCNTs mixed solution, four sample solutions were prepared in the ratio of 1:0, 1:1, 1:2 and 2:1 according to the material's mass. 2 mg

of C[8]1 was dissolved in 10 mL chloroform to produce 0.2 mg/mL concentration sample solution under 10 min of ultrasonication process (40 kHz). Then, MWCNTs were added into the solution and ultra-sonicated for 3 h to ensure a homogeneous solution. Long hours of ultrasonication aided in mechanical cutting of CNTs' long chain (Mermer et al. 2012). A similar process was performed for C[8]2.

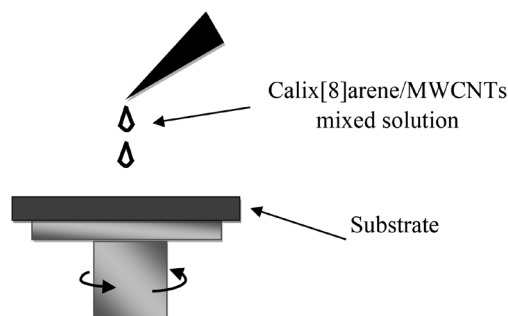


FIGURE 2. Calix[8]arene/MWCNTs thin film formation using spin coating deposition technique

Spin coater Model WS-400BZ-6NPP/A1/AR1 was used to form calix[8]arene/MWCNTs thin films as illustrated in Figure 2. Ten drops of prepared solution were dropped onto a clean substrate in the spin coater to ensure uniform thin film formation. Then, the substrate was spun at a speed of 3000 rpm for 15 s to develop one layer of thin film. The dropping and spinning process were repeated until the desired layers achieved. Thin film of 10 and 20 layers were developed for each prepared solution, respectively. The thin film was heated in an oven for 20 min at  $80^\circ\text{C}$  to eliminate the chloroform residue. Similar procedure was followed by the other prepared solutions to deposit thin films.

### CHARACTERIZATION PROCESS

The  $\Pi$ -A isotherms of C[8]1 and C[8]2 solutions were determined with a KSV 2000 system Langmuir-Blodgett (LB) deposition trough. Deionized water ( $18.2 \text{ M}\Omega$ ) was used as subphase and have been purified by Millipore Milli-Q system. Wilhelmy plate made from filter paper acted as the pressure sensor. Isotherms of C[8]1 and C[8]2 solutions were elucidated using different volumes. Speed for movable barriers was 12 mm/min. The sensitivity is  $\pm 0.1 \text{ mN/m}$  for surface pressure and  $\pm 0.01 \text{ \AA}^2/\text{molecule}$  for the molecular area.

The prepared calix[8]arene/MWCNTs thin films on Si substrate were characterized using KSV Surface Potential Meter (SPOT) with a vibrating plate condenser connected to the counter electrode that was located under the thin films to determine the surface potential. Uniform distances (1 - 2 mm) were ensured between the SPOT and samples under room temperature. The sensitivity is  $\pm 1 \text{ mV}$ .

Finally, the conductivity properties of the thin films were determined by four-point probe Keithley 2636A and

Leios TMXpert software under 27°C from -5 V to 5 V. Before the conductivity characterization process, samples on ITO substrates (surface resistivity of 8 - 12  $\Omega$ /sq) were coated with 60 nm gold layer as metal contact to improve the flow of current using electron beam thermal evaporator. Thickness of thin films were determined through surface profiler.

## RESULTS AND DISCUSSION

### SURFACE PRESSURE-AREA ( $\Pi$ -A) ISOTHERM

Calix[8]arene monolayers were studied through isotherm graphs that displayed the surface pressure as a function of the molecular area at the air-water interface. Different volumes of C[8]1 (75, 100, 125, 150)  $\mu$ L with identical concentration were spread dropwise onto the subphase by using a Hamilton microsyringe. 15 min were allowed for the solvent to evaporate before measurements were collected. Same procedures were performed for C[8]2. Repeated measurements of both indicated good stability and reproducibility of the monolayers.

In Figure 3, both calix[8]arenes formed stable monolayers until 40 mN/m when the monolayers started to collapse. Increasing the loading volume of calix[8]arene directly shifted the isotherm curve to left in both cases. For both 75  $\mu$ L of calix[8]arenes, the isotherms were not entirely formed due to incomplete monolayer formation caused by low quantity of calix[8]arenes. The direct phase transition from liquid-expanded state to liquid-condensed phase ( $\sim$ 1-20 mN/m), followed by solid phase ( $>$ 20 mN/m)

before the collapse were observed. Similar isotherm graphs were observed by others (Çapan et al. 2010; Razali et al. 2015b). Flexures at around 40 mN/m in C[8]1 isotherm, is similar as reported in others (Davis et al. 1996; Ozmen et al. 2014). The increment of surface tension stimulated change in molecules conformation and caused certain molecules to slip out from the monolayer, thus result in the flexure formation (Ozmen et al. 2014). The limiting area per molecule shown in Table 1 were determined by extrapolating the steepest linear part of the curves in the solid phase. The radius of molecules was calculated from the limiting area per molecule by considering the area of circle taken on the air-water interface. The radius of C[8]1 molecule has a higher value than C[8]2, mainly due to the bulky lower rim. Both calix[8]arene monolayers have the general isotherm characteristics, but the signature of isotherm graphs are different.

### SURFACE POTENTIAL ISOTHERM

Surface potential ( $\Delta V$ ) is recorded through the vibration of air between the vibrating plate and monolayer that resulted in the capacitance change between the air gap of two surfaces, caused alternating current induction to flow in external circuit (Leblanc & Huo 2006). For this study,  $\Delta V$  between the vibrating plate and thin film was obtained by subtracting the  $\Delta V$  of vibrating plate and bare substrate from  $\Delta V$  of vibrating plate and thin film on substrate. For each sample, the maximum surface potentials ( $\Delta V_{\max}$ ) were recorded for 10 and 20 layers for comparison.

In Table 2 and Figure 4, a significant increase in  $V_{\max}$  occurred in both 10 layers and 20 layers samples.

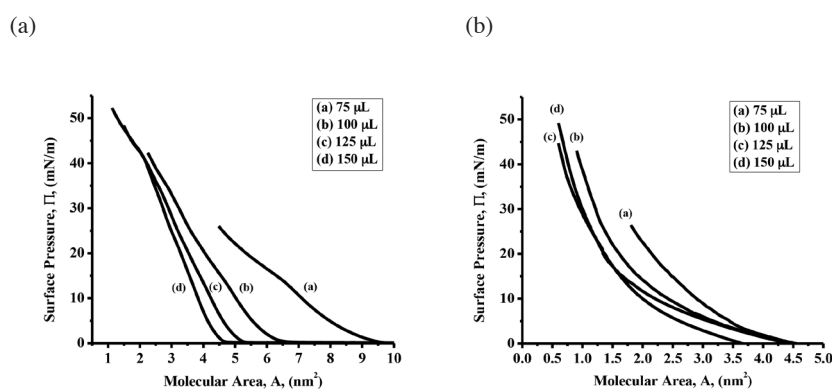


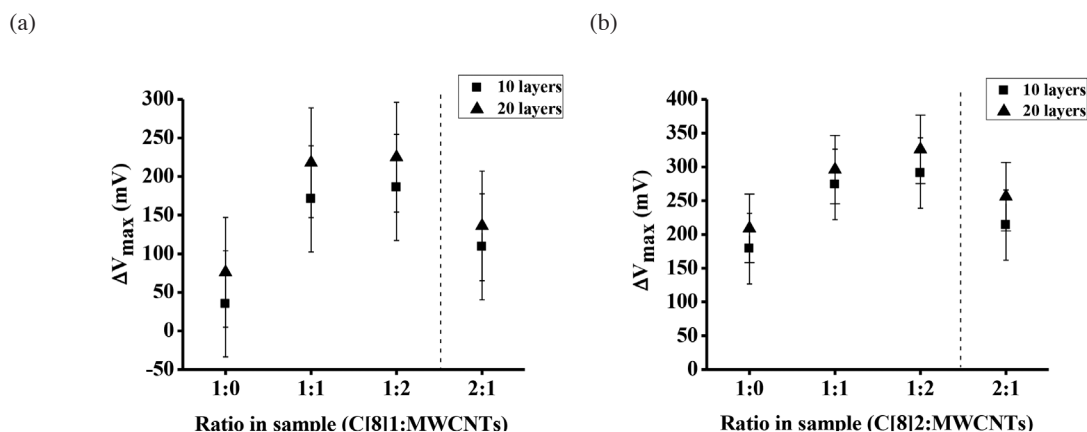
FIGURE 3. Isotherm graphs of (a) C[8]1 and (b) C[8]2

TABLE 1. Limiting area per molecule and radius of C[8]1 and C[8]2

Volume ( $\mu$ L)	Limiting Area Per Molecule ( $\text{nm}^2$ )		Radius (nm)	
	C[8]1	C[8]2	C[8]1	C[8]2
75	8.21	3.14	1.617	1.000
100	5.47	1.91	1.320	0.780
125	4.74	1.55	1.228	0.702
150	4.32	1.50	1.173	0.691

TABLE 2. Surface potential for C[8]1/MWCNTs thin films and C[8]2/MWCNTs thin films

Ratio In Sample Calix[8]arene : MWCNTs	$\Delta V_{\max}$ (mV)			
	C[8]1/MWCNTs Thin Film		C[8]2/MWCNTs Thin Film	
	10 Layers	20 Layers	10 Layers	20 Layers
1:0	35	179	76	209
1:1	171	274	218	296
1:2	186	291	225	326
2:1	109	214	136	256

FIGURE 4. Maximum surface potential,  $\Delta V_{\max}$  versus ratio in sample (a) C[8]1/MWCNTs and (b) C[8]2/MWCNTs thin films

The increment in thickness of films due to the number of deposited layer and amount of nanomaterial contributed to the increment of  $V_{\max}$ . For each specific layer, the higher value of  $\Delta V_{\max}$  was demonstrated by calix[8]arene/MWCNTs in ratio of 1:2 where the mass of MWCNTs is doubled than that of calix[8]arene. In the ratio of 2:1 for both calix[8]arene:MWCNTs, the  $V_{\max}$  decreased as compared to calix[8]arene:MWCNTs (1:1) but still higher than calix[8]arene:MWCNTs (1:0). This demonstrated that  $V_{\max}$  of calix[8]arene indeed has increased due to the presence of MWCNTs. Surface potential of C[8]2 displayed higher values when compared with C[8]1 in all ratios.

#### CONDUCTIVITY PROPERTY

For conductivity property, thin films that consist of 10 layers were compared between both calix[8]arenes. The average resistivity of thin films was obtained through four-point probe technique. The conductivity,  $\sigma$  was calculated for each using simple conductivity formula.

Naturally, calixarene has very low conductivity and is difficult to measure (Chaâbane et al. 1994) as shown with no value in Table 3. However, the combination of calixarene with the outstanding conductivity of MWCNTs would reserve the superior properties of both through interaction, thus developing more sensitive calix[8]arenes thin film. The conductivity of the thin film was increased with higher ratio of MWCNTs in the sample as expected since MWCNTs are conductors that ease the

electron transfer. This result is in parallel with the other studies (Özbek et al. 2013; Wang et al. 2015, 2012). For ratio of 2:1 in both calix[8]arene:MWCNTs thin films, the conductivity has decreased significantly compared to calix[8]arene:MWCNTs (1:1) due to increased amount of calix[8]arene. For each sample, the conductivity for C[8]2/MWCNTs thin films was higher than C[8]1/MWCNTs thin films as displayed in Figure 5.

Morphology of calix[8]arene/MWCNTs composites have been visualized in Supian et al. (2013) and Razali et al. (2015a, 2015b). Since C[8]2/MWCNTs thin films gave higher value of  $\Delta V_{\max}$  and conductivities as compared to C[8]1/MWCNTs thin films, assumption have been made that these results were due to preference of MWCNTs contacted better with C[8]2, resulted from type of orientation for the attachment of C[8]2 to MWCNTs. Calix[8]arenes may have attached to MWCNTs in two major possible orientations, perpendicular or parallel which both orientations gave advantages to C[8]2. In the former orientation, C[8]2 can binds closer to the MWCNTs due to shorter lower rim and lack of upper rim; while in both orientations, small-sized C[8]2 occupies less surface area when bonded to MWCNTs, resulted in more C[8]2 per area in contact as compared to bulky C[8]1. More contact exists in both orientation result in better conductivity. However, it is difficult to visualize the ideal orientation of calix[8]arenes since other orientations may exist such as visualized in others (Wang et al. 2012).

TABLE 3. Resistivity, conductivity and thickness of C[8]1/MWCNTs thin films and C[8]2/MWCNTs thin films

Ratio in sample Calix[8]arene : MWCNTs	Resistivity, $\rho$ ( $\Omega$ )		Conductivity, $\sigma$ ( $\mu\Omega^{-1}\text{m}^{-1}$ )		Thickness, h ( $\mu\text{m}$ )	
	C[8]1 / MWCNTs	C[8]2 / MWCNTs	C[8]1 / MWCNTs	C[8]2 / MWCNTs	C[8]1 / MWCNTs	C[8]2 / MWCNTs
1:0	-	-	-	-	12.76	12.20
1:1	16554.36	13870.49	60.407	72.096	16.48	14.36
1:2	3320.39	1071.55	301.169	933.228	22.66	20.18
2:1	24483.97	14642.58	40.843	68.294	20.23	16.75

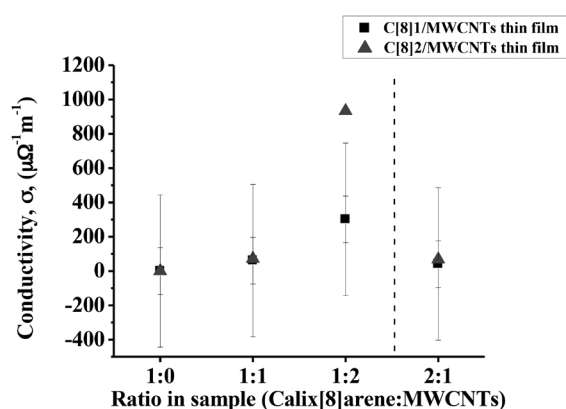


FIGURE 5. Conductivity of different ratio of C[8]1/MWCNTs thin films and C[8]2/MWCNTs thin films

Non-covalent interactions like van der Waals interactions may have highly occurred between calix[8]arene and MWCNTs while hydrogen bonding may present between the adjacent calix[8]arenes (Liu et al. 2008) in this study. In spite of the occurrence, covalent bonding also may exist between both (Wang et al. 2012) although some (Star et al. 2003) stated that covalent modification on CNTs may possibly destruct the physical properties of CNTs. This situation indeed occurred in Wang et al. (2012) where crystallinity of CNTs declined, but the result remains good. The incorporation of calix[8]arene with MWCNTs in this study has been shown with Fourier Transform Infrared spectra and reported previously (Razali et al. 2015a).

As reviewed in Zhu and Fang (2014), molecular recognition and signal transduction are two major phases occurred in the supramolecular electronic sensor. Hence, one of the vital properties of a good sensor is regarding about the transduction of host-guest interaction effectively into modulation of potential, current or resistance. By enhancing the conductivity of the respective host such as calix[8]arene in this case, the signal transduction process can be more efficient, result in a more sensitive sensor. Table 4 lists some findings about the combination of calixarene and CNTs for comparison about this work and others reported in literature.

## CONCLUSION

In summary, the conductivity of calix[8]arene thin films has been successfully enhanced with MWCNTs through spin coating deposition method. Monolayers of calix[8]arenes, C[8]1 and C[8]2 were compared using isotherm graphs before they were mixed with MWCNTs in various ratio. Then, the mixed solutions were spin-coated onto substrates and characterized for surface potential and conductivity. C[8]2/MWCNTs thin films demonstrated higher surface potential values and better conductivities than C[8]1/MWCNTs thin films. From the results, we may concluded that the conductivity property of the calix[8]arene-MWCNTs composite is influenced from two aspects, first one is the combination ratio between the two materials, whilst the second one is the structure of the calix[8]arene.

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