

RESEARCH PAPER

Raman, FTIR, UV-Visible and FESEM Studies on Calix[8]arene Embedded Multi-walled Carbon Nanotubes Nanocomposites using Spin Coating Technique

Amira Shakila Razali¹, Faridah Lisa Supian^{1,*}, Abdullah F. Al Naim²,
Shahrul Kadri Ayop¹, Noor Azyyati Azahari¹

¹Department of Physics, Faculty of Science and Mathematics, Universiti Pendidikan Sultan Idris, 35900, Tanjong Malim, Perak, Malaysia

²Department of Physics, College of Science, King Faisal University, P.O. Box 400, Al-Ahsa 31982, Saudi Arabia

*Corresponding author: faridah.lisa@fsmpt.upsi.edu.my

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Abstract

In this research, the preparation and characterization of the organic compound calix[8]arene (TBC8) are embedded with multi-walled carbon nanotubes (MWCNTs) using spin coating technique. The nanocomposites were prepared layer by layer, where TBC8 was dissolved in chloroform solution (0.2 mg/mL), followed by the additional layer of MWCNTs in the upper nanocomposites. We have explored the effects of TBC8 being modified with MWCNTs by Raman, where the crystallinities of the nanocomposites were observed. By Fourier Transform Infrared (FTIR) analysis, the nanocomposites' characteristic patterns have been detected. Ultraviolet-visible spectroscopy defines the fingerprints and the shifting of the nanocomposites while Field Emission Scanning Electron Microscope (FESEM) determines the structural morphology. The TBC8 attached to the MWCNTs has a future potential application for the development of the sensor in pollutant monitoring nano-electronics devices.

Keywords: Calix[8]arene; Multi-walled carbon nanotubes (MWCNTs); Nanocomposites; Raman; FESEM; UV-Visible

INTRODUCTION

One of the environmental concerns is water contamination by heavy metals because of the possible harmful toxic effects of metal ions, especially threats towards aquatic life, human beings and the environment (Deligoz & Memon, 2011). Several processes have been used to eliminate metal ions from water, such as chemical precipitation, ion exchanges, adsorption processes and reverse osmosis (Stafiej & Pyrzynska, 2007). However, some of these processes are often associated with many problems, which make their use ineffective, high operational costs and the inability to eliminate the heavy metals to the acceptable levels (Agustiono et al., 2006).

The increasing awareness on control of the level on the environmental pollutants has sparked an interest towards the development of novel sensors, more selective and effective removing metal ions from water and soils (Clevenger, 1990). In this regard, supramolecular chemistry has offered a comprehensive better solution for eliminating toxicity. As a result, calixarene could be an ideal backbone for developing sensors to recognize ionic species at the molecular level. Calixarenes recently attracted appreciable attention because of their potential to mimic enzymes.

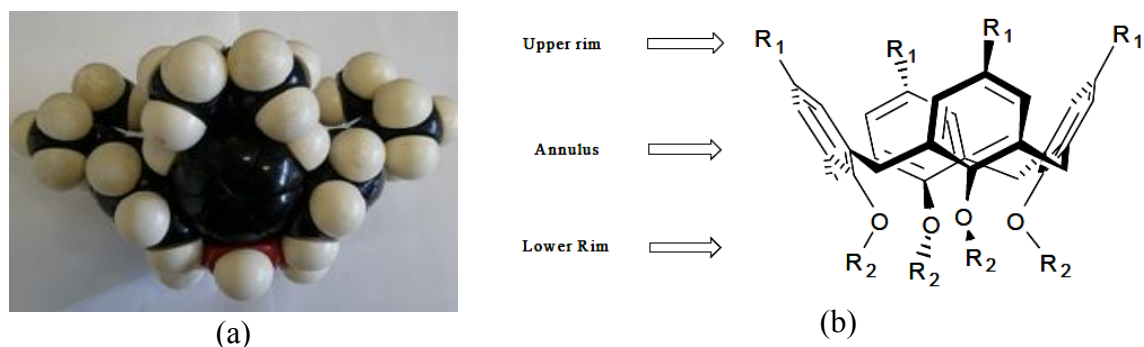


Figure 1. (a) CPK modeling of calixarene and (b) Schematic representation of 'upper' and 'lower' rim of calix[4]arene (Gutsche, 1989).

Calixarene is a macrocyclic oligomer obtained as a product of hydroxyalkylation between formaldehyde and phenols (Gutsche, 1989). Calixarene exists in a bowl- or vase-like conformation. It also offers the possibility to incorporate "guest" molecules similar to other macrocyclic compounds. Promise selective and helpful complexation agents in calixarenes offers much interest to explore its broad applicability (Mohd Azmi et al., 2020, Supian et al., 2010; Mamba et al., 2010; Hasalettin & Shahabuddin, 2011; Capan et al., 2010). Hence, various novel calixarene derivatives have been synthesized via the modification of the lower (hydrophilic) or upper (hydrophobic) rim of calixarenes. The lower and the upper rim, which offers such modification, are shown in Figure 1 (Uysal et al., 2002; Leeuwen et al., 2002; Akkus et al., 2003).

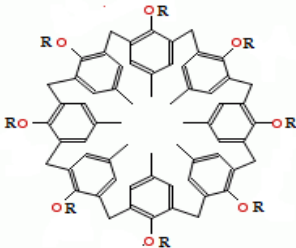
Carbon nanotubes (CNTs) have been widely utilized as absorbents to eliminate pollutants from water in recent years (Hussain et al., 2012; Dilip et al., 2009; Arun et al., 2011). The distinct properties of carbon nanotube such as large specific area, hollow-and-layered structures, high mechanical strength, and high thermal stabilities make them a suitable candidate as an absorbent, leading to great promising applications in environmental protection (Leeuwen et al., 2002). Gao et al., 2017, has reported the CNTs and Calix[8]arenes nanocomposites on their external stimuli response properties. A hybrid-based sensor project on single-walled carbon nanotubes (SWCNTs) with Calixarene has been successfully done towards VOCs (Sarkar et al., 2018).

This work attempts to explore these effects on multi-walled carbon nanotubes (MWCNTs) by modified on novel calix[8]arene by using the spin coating technique. This project emphasizes that MWCNTs were purposely chosen to increase Calixarene's conductivity as they are known as highly insulating (Lim et al., 2020). The following sections present the experimental details of sample preparation and characterization results obtained FESEM, UV-Visible, FTIR and Raman spectroscopy.

MATERIALS AND METHODS

The MWCNTs used in this study were multi-wall type CNTs with a 10 to 20 nm diameter and a structural length of less than 1 μ m. These nanotubes were obtained from Shezen Nanotech, China. A type of Calix[8]arene (TBC8) was selected as a base molecule, and the details are given in Table 1.

Table 1. Details on the Calix[8]arene

Material	IUPAC nomenclature	Molecular weight (g/mol)	Molecular structure
Calix[8]arene (TBC8)	5,11,17,23,29,35,41,47-p-tert-butyl-49,50,51,52,53,54,55,56-calix[8]arene	1762.11	 <p>R=(CH₂)₅COOH</p>

Synthesis of Calixarene-CNT Solutions and Films

TBC8 powder of 2.0 mg was dissolved in 10 mL of chloroform (CHCl₃) as a solvent to produce a 0.2 mg/mL concentration solution. The solution was then sonicated for 60 minutes in an ultrasonic bath at frequency of 40 kHz and room temperature. An exact amount of 2.0 mg of MWCNTs was added into each uniformly solved TBC8 solution, and the sonication process was applied for another 7 hours to these solutions. The TBC8-MWCNTs were kept for 24 hours at room temperature.

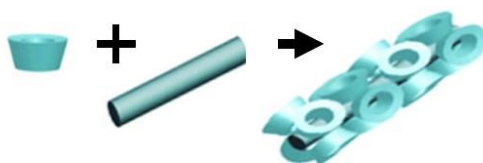


Figure 2. The illustration of mechanism hybrid calix[8]arene-MWCNTs

We then prepared these thin-film samples TBC8-MWCNTs (as in Figure 2) using a spin coating method (spin coater Model WS-400BZ-6NPP/A1/AR1). The TBC8-MWCNTs nanocomposites were deposited layer by layer on a silicon substrate (1.0 \times 1.0 cm) with a spin speed of 3000 rpm. The acceleration time was 15.0 s and ten drops per sample were done on the nanocomposites.

Characterization of Nano-composites Calix[8]arene-MWCNTs

The hybrid nanocomposites TBC8-MWCNTs were further analyzed and characterized. Raman data was obtained using a Renishaw inVia Raman Microscope at 488 nm wavelength by Argon laser. Fourier transform infrared (FTIR) spectra of thin films were measured using a Nicolet 6700 FTIR spectrometer from 400 to 4000 cm⁻¹ (nominal resolution of 4 cm⁻¹). The UV-Visible spectra of TBC8-MWCNTs were determined on a JASCO V-750 UV-Vis spectrometer

using quartz cell with a 1 cm optical path length from 190 to 800 nm in absorbance mode. Field emission scanning electron microscope (FESEM) enables visualization of the morphology of the surface model Hitachi SU 8020 UHR.

RESULTS AND DISCUSSION

Raman Spectroscopy

Raman spectroscopy was used to investigate the effect of TBC8 on MWCNTs crystallinity. The characteristics bands observed are tangential mode (G-band) and disordered mode (D-band). The tangential mode (G-band) at $1540\text{--}1600\text{ cm}^{-1}$ are the most intense high-energy modes of nanotubes correspond to crystalline graphitic structures. The disorder modes (D-band) around $1270\text{--}1350\text{ cm}^{-1}$ correspond to the sp^2 - hybridized carbon atom, which is correlated to the extent of nanotube sidewall defects and chemical sidewall functionalization (Li et al., 2006). The Raman spectra are covering the entire frequency range from 100 to 4000 cm^{-1} were recorded at room temperature using a micro Raman spectrometer equipped with a 457 nm laser.

Figure 3(a) shows typical Raman spectra for CNTs, where certainly one could observe the fingerprints of MWCNTs. The spectra are composed of ordinary to peak at around 1582 cm^{-1} for graphite (G) peak and around 1352 cm^{-1} for defect (D), which generally arises in sp^2 Carbon samples containing pores, impurities, or other breaking defects (Makayonke, 2011).

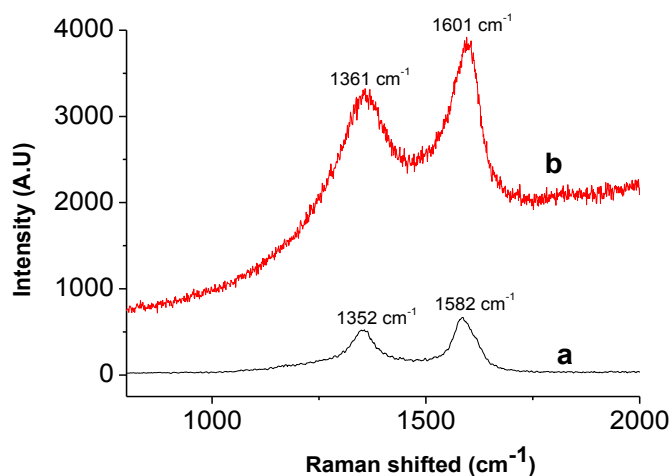


Figure 3. Raman spectra of (a) multi-walled carbon nanotubes (MWCNTs) and (b) nanocomposites TBC8-MWCNTs

The intensity of peak at $1350\text{--}1370\text{ cm}^{-1}$ regions increase on modification with Calixarene as seen in Figure 4(b). This indicates an abundant content of sp^3 hybridized Carbon associated with the disruption of the aromatic system of the π electron on the nanotube walls (Ling et al., 2009). In the high-frequency range from 1000 to 2000 cm^{-1} , the G-band peak for the nanocomposite shifted from 1582 cm^{-1} to the higher wavenumber of 1590 cm^{-1} . This indicates the presence of interaction between the calix[8]arene in carbon nanotubes surface. Definitely, the MWCNTs and TBC8-MWCNTs peaks are located on similar Raman shift values, but the I_D/I_G ratio will be different as composites tend to boost the amorphous structures (Lim et al., 2020).

Fourier Transform Infrared (FTIR) Spectroscopy

Figure 4 shows the FTIR spectra of (a) MWCNTs (blue line) (b) TBC8 (red line) and (c) TBC8-MWCNTs (purple line).

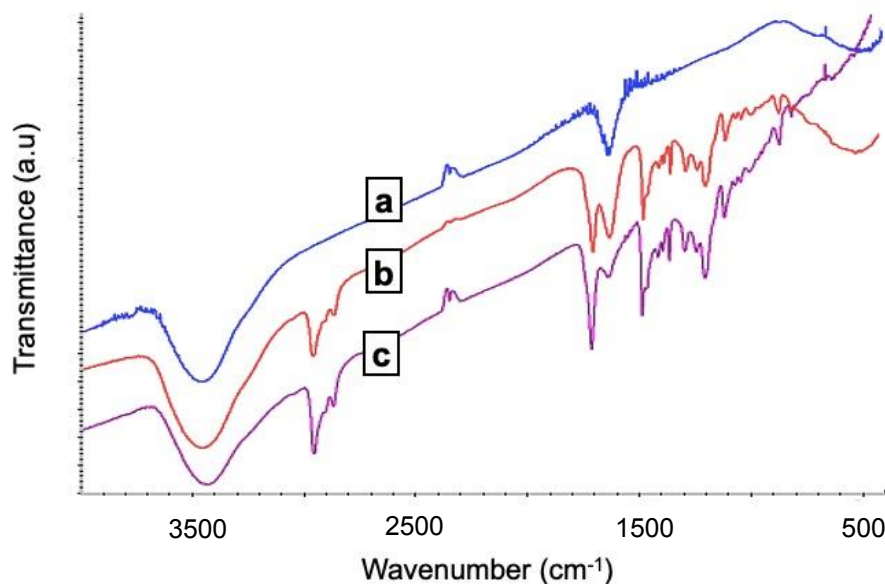


Figure 4. FTIR spectra of (a) MWCNTs (blue line) (b) TBC8 (red line) and (c) TBC8-MWCNTs (purple line)

From Figure 4, FTIR studies have been performed in the range 400 to 4000 cm^{-1} . FTIR spectra from the as-received MWCNTs (Figure 4(a)) show a broad peak at 1630 cm^{-1} which refers to stretching vibrations of the six-membered ring of Carbon (C). The peak at 1630 cm^{-1} is assigned to the C-H of C=C-H or aromatic rings.

The spectrum of TBC8 has an absorption band at 2959 cm^{-1} and 2868 cm^{-1} for $\text{C}(\text{CH}_3)_3$, while the peak at 1708 cm^{-1} assigned to carbonyl groups, C=O stretching, which was introduced by the carboxylation of the TBC8. The peaks between 1116 and 1203 cm^{-1} in Figure 4 are due to C-O stretching bands of the phenol. Also, spectra of TBC8 exhibit typical bands originating from $-\text{CH}_2$ rocking at 748 cm^{-1} presence of a long-chain alkyl molecule. A new peak is observed at 818 and 638 cm^{-1} which attributed to the overlapping of a signal from the C-H of TBC8 on MWCNTs functionalized material. FTIR analysis is indecisive in confirming the interaction mode of the calixarene at the surface of the nanotubes (Li et al., 2006)

UV-Visible Spectroscopy

Figure 5 shows the typical UV-Visible absorption spectra of TBC8 and TBC8-MWCNTs film in chloroform. The absorption spectra exhibit a peak at 210 nm of TBC8, and it is attributed to the π - π^* transition, which denotes the electronic transition in calixarenes; the electron's elevation from the π bonding orbital to the π^* antibonding orbital. The general shape of the absorption spectra is the same for hybrid TBC8-MWCNTs.

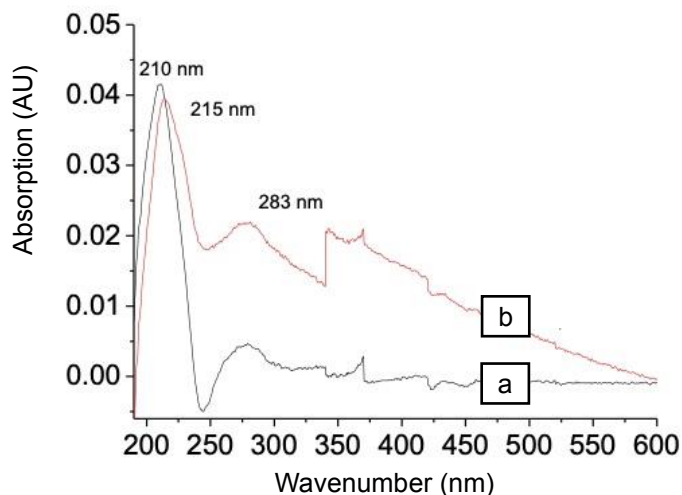


Figure 5. UV-Vis spectra of (a) TBC8 (b) hybrid nanocomposite TBC8-MWCNTs

Noticeably, the hybrid TBC8-MWCNTs shoulder is shifted to the right around 215 nm (Figure 5(b)). This shift in the film's absorption band most feasibly the result of molecular aggregation taking place during film formation, for which the wavelength increases while energy reducing. Similar results have been found using Calixarene modified MWCNTs (Dharamvir et al., 2010). The shift indicates the presence of interaction between MWCNTs and TBC8 on the external surface.

Field Emission Scanning Microscope (FESEM)

FESEM detected the morphology of the TBC8-MWCNTs hybrid. The FESEM micrographs of the sample (Figure 6) show that the formation of TBC8 on the exterior walls of MWCNTs has an apparent influence on the morphology of the sample. The bumpiness and inconsistency of TBC8-MWCNTs outer walls are noticeable in Figure 6(b).

The composition of TBC8-MWCNTs is further analyzed by energy-dispersive X-ray (EDX). The spectra show the presence of peaks Carbon (C), Oxygen (O) and Silicon (Si) elements, which substantiate with the molecular components of TBC8. The TBC8 is abundantly made up of Carbon as it is a type of Calix[8]arenes.

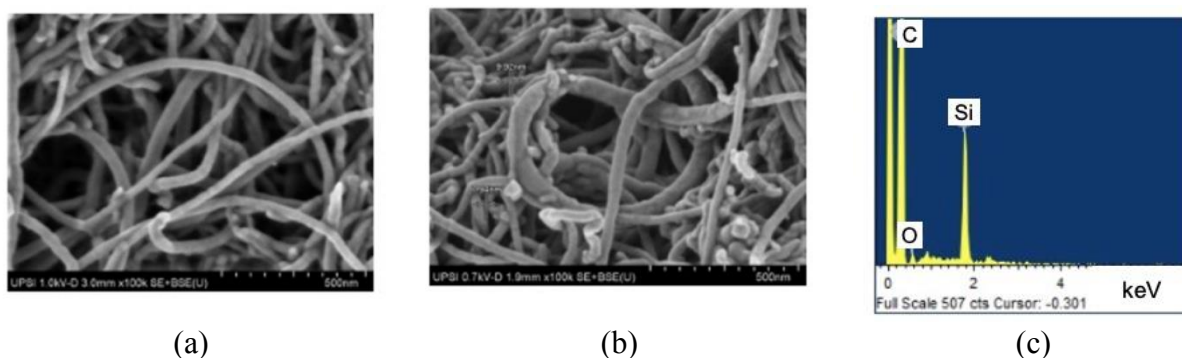


Figure 6. SEM images and EDX spectra of (a) MWCNTs (b) TBC8-MWCNTs (c) EDX analysis

CONCLUSION

In summary, Raman, FTIR, UV-Visible and FESEM investigation on MWCNTs of calix[8]arene has been revealed. The preparation and characterization of modification TBC8 and MWCNTs were presented by the Raman result, where TBC8 in MWCNTs have altered hexagonal structure carbon nanotubes and high-quality crystallinity of carbon nanotubes. Fourier Transform Infrared (FTIR) spectroscopy studied shown the new peak is observed at 818 and 638 cm^{-1} which is attributed to the overlapping of a signal from the C-H of TBC8 on MWCNTs functionalized material. The absorption band of TBC8-MWCNTs observed at 210 nm were shifted to the red range of 215 nm. The redshift indicated the presence of interactions between TBC8 on the outer walls of MWCNTs. FESEM study showed that the formation of TBC8 on the outer walls of MWCNT is apparently visible on the morphology of the sample. Energy dispersive X-ray (EDX) spectra on TBC8-MWCNTs displayed a higher percentage of O and C peaks which confirmed the incorporation of TBC8 with MWCNTs.

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REFERENCES

- Agustiono, K.T., Chan, G.Y.S., Lo, W.H. & Babel, S. 2006. Comparison of low-cost adsorbents for treating wastewater with heavy metal - A Review. *Science Total Environment*, 366, 409-426
- Akkus, G.U., Memon, S., Sezgin, M., & Yilmaz, M. 2003. A versatile approach toward calix (aza) crown oligomers: Synthesis and metal ion extraction. *Journal of Macromolecular Science, Part A*, 40(2), 95.
- Arun P.P., Singying Y. & Shen M.C. 2011. Preparation and Characterization of Bismuth Oxide Nanoparticle-Multiwalled Carbon Nanotube Composite for the Development of Biosensor. *Talanta*, 87, 15-23.
- Çapan, R., Özbek, Z., Göktaş, H., Şen, S., İnce, F. G., Özel, M.E. & Davis, F. 2010. Characterization of Langmuir-Blodgett films of a calix [8] arene and sensing properties towards volatile organic vapors. *Sensors and Actuators B: Chemical*, 148(2), 358-365.
- Clevenger, T.E. 1990. Use of sequential extraction to evaluate the heavy metals in mining wastes. *Water, Air, and Soil Pollution*, 50(3-4), 241-254.
- Deligz, H., & Memon, S. 2011. Overview on Metal Cations Extraction by Azocalixarenes. *Pakistan Journal of Analytical & Environmental Chemistry*, 12(1 & 2), 24.
- Dharamvir, K., Jeet, K., Du, C.S., Pan, N., & Jindal, V.K. 2010. Structural modifications of multi-walled carbon nanotubes by swift heavy ions irradiation. *International Journal of Nano Research*, 10, 1-9.
- Lim, D.C.K., Supian, F.L. & Hamzah, Y., 2020. Langmuir, Raman, and electrical properties comparison of Calixarene and calixarene-rGO using Langmuir Blodgett (LB) technique. *Journal of Materials Science*, 31, 18487-18494
- Gao, M., Li, L., Qiu, J., Zhang, X., He, X., Lv, S., Ma, X., & Li, G. 2017, Nanocomposites of Carbon Nanotube/Polyaniline with Pending Calix[8]Arene and their External Stimuli Response Properties. *Materials Science Forum*, 898, 2286-2293.
- Gutsche, C.D., (Ed.), 1989. Calixarenes in Monographs in Supramolecular Chemistry, Royal Society of Chemistry 127.
- Hussain, S., Jha, P., Chouksey, A., Raman, R., Islam, S.S., Islam, T., & Choudhary, P. K. 2011. Spectroscopic investigation of modified single wall carbon nanotube (SWCNT). *Journal of Modern Physics*, 2(06), 538-543.
- Li Y.H., Zhu Y.Q., Zhao Y.M., Wu D.H. & Luan Z.K. 2006. Matter. *Diamond Relative*. 15, 90.
- Ling, I., Alias, Y., Makha, M., & Raston, C. L. 2009. Water solubilization of single-walled carbon nanotubes using p-sulfonatocalix [4] arene. *New Journal of Chemistry*, 33(7), 1583-1587.

- Makayonke M.T. 2011. The Use of Carbon Nanotubes Co-Polymerized with Calixarenes for the Removal of Cadmium and Organic Contaminants from Water. Masters Theses, University of Johannesburg
- Mamba, G., Mbianda, X.Y., Govender, P.P., Mamba, B.B., & Krause, R.W. 2010. Polymers in the Removal of Heavy Metals from Water. *Journal of Applied Sciences*, 10(11), 940-949.
- Mohd Azmi, M.S., Noorizhab, M.F.F., Supian, F.L., Malik, S.A. 2020, A Review of Calixarene Langmuir–Blodgett Thin Film Characteristics for Nanosensor Applications. *Defence S and T Technical Bulletin*, 13, 205-216
- Sarkar, T., Srinives, S., Rodriguez, A., & Mulchandani, A., 2018. Single-walled Carbon Nanotube-Calixarene Based Chemiresistor for Volatile Organic Compounds. *Electroanalysis*, 30, 2077 – 2084
- Singh, D.K., Iyer, P.K., & Giri, P.K. 2009. Optical signature of structural defects in single walled and multi-walled carbon nanotubes. *Journal of Nanoscience and Nanotechnology*, 9(9), 5396-5401.
- Stafiej, A., & Pyrzynska, K. 2007. Adsorption of heavy metal ions with carbon nanotubes. *Separation and Purification Technology*, 58(1), 49-52.
- Supian, F.L., Richardson, T.H., Deasy, M., Kelleher, F., Ward, J.P., & McKee, V. 2010. A surface potential study of ion-uptake by 5, 11, 17, 23-tetra-tert-butyl-25, 27-diethoxycarbonyl methyleneoxy-26, 28, dihydroxycalix [4] arene and 5, 17-(3-nitrobenzylideneamino)-11, 23-di-tert-butyl-25, 27-diethoxycarbonyl methyleneoxy-26, 28-dihydroxycalix [4] arene Langmuir Blodgett (LB) monolayers. *Sains Malaysiana*, 39(3), 423-433.
- Uysal, G., Memon, S. & Yilmaz, M. 2002. *Polycyclic Aromat. Compound*. 221075
- Van Leeuwen, F. W., Beijleveld, H., Kooijman, H., Spek, A. L., Verboom, W., & Reinhoudt, D.N. 2002. Cation control on the synthesis of pt-butylthiacalix [4](bis) crown ethers. *Tetrahedron letters*, 43(52), 9675-9678.