

Synthesis and characterization of thiacalix[3]triazine and 1,3,5-tris(4-bromophenyl)benzene for chemsensor application

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(Received on 15th June 2017, accepted on 26th June 2017)

ABSTRACT

The synthesis of thiacalix[3]triazines and 1,3,5-tris(4-bromophenyl)benzene have been synthesized via simple steps and was characterized to determine the chemical structure. The structure of Thiacalix[3]triazines was characterized via ¹H NMR and ¹³C NMR that conformed the expected structure of compound. In addition, the thiacalix[3]triazines

exhibited the λ_{max} at 560 nm and λ_{onset} at 720 nm which corresponding to the bandgap of 1.7 eV. Thiacalix[3]triazines, cyclotrimeric metacyclophanes with direct S linkages between the heteroaryl constituents, were shown to associate with anion that could be useful for chemsensor application.

Keywords: 1,3,5-tris(4-bromophenyl)benzene, chemsensor, conjugated polymer, heteroaryl, thiacalix[3]triazines

INTRODUCTION

Heterocalixarenes have gained considerable attention in recent years due to their potential value in supramolecular chemistry. In particular, thiacalix[3]triazine is a kind of class of calixarenes which have been proven to be suitable macrocyclic scaffolds depend on anion binding moieties [1]. The heteroatom bridges allow tuning of the macrocycle size, the electron density on the arene building blocks and the preferred conformation provide additional binding sites towards a perfect (induced) fit of a desirable guest molecule. Among these heterametacyclophanes, the thia analogues or thiacalixarenes have been studied most intensively and they are widely recognized as effective receptors for small organic compounds and heavy/transition metals [1-3]. The fields of oxa- and azacalixarenes have also steadily grown [4-10], both in synthetic scope and supramolecular applications. However, extension of heterocalixarene chemistry to the larger group

through chalcogen elements was noticeably absent in the literature until a very recent communication on.

Thiacalix[3]triazine is constructed from 1,3,5-triazines, enforced as electron-deficient host for halide ion binding through anion- π interactions [10]. Thiacalix[3]triazine can be prepared by condensation of a dichloro-1,3,5-triazine with sulfide ion. The synthesis of thiacalix[3]triazines with peripheral phenol or *tert*-butyl substituents from the reaction of corresponding 2,4-dichloro-1,3,5-triazine with NaSH or alternatively Na₂S has been reported. Thiacalix[3]triazine has been shown to interact with non-protic and less-acidic protic anions via the anion association mechanism, and with more-acidic protic anions following the protonation mechanism

In this contribution, here we report the synthesis and characterization of thiacalix[3]triazine and its potential application as chemsensor for detecting of anion in the environment.

MATERIAL AND METHOD

Materials

Cyanuric chloride (99.8 %), phenol (99.8 %), NaSH (99 %), potassium acetate (KOAc), sodium carbonate (99 %) and magnesium sulfate (98 %) were purchased from Acros (Bridgewater, NJ, USA) and used as received. Chloroform (CHCl₃) (99.5 %), toluene (99.5 %) and tetrahydrofuran (THF) (99 %) were purchased from Fisher/Acros (Bridgewater, NJ, USA) and dried using molecular sieves under N₂. Dichloromethane (CH₂Cl₂) (99.8 %), *n*-heptane (99 %), methanol (99.8 %), ethanol (99.8 %), ethyl acetate (99 %) and diethyl ether (99 %) were purchased from Fisher/Acros (Bridgewater, NJ, USA) and used as received.

Characterization

¹H NMR and ¹³C NMR spectra were recorded in deuterated chloroform (CDCl₃) with tetramethylsilane as an internal reference, on a Bruker Avance 300MHz. Fourier Transform Infrared (FTIR) spectra, collected as the average of 64 scans with a resolution of 4 cm⁻¹, were recorded from a KBr disk on the FTIR Bruker Tensor 27. UV-visible absorption spectra of polymers in solution and polymer thin films were recorded on a Shimadzu UV-2450 spectrometer over the wavelength range 300–700 nm. Fluorescence spectra were measured on a Horiba IHR 325 spectrometer.

Synthesis of 2,4-dichloro-6-phenoxy-1,3,5-triazine

Cyanuric chloride (7) (1.840 g, 10 mmol) was dissolved in acetone (100 mL) and cooled to 0 °C. In a separate flask, phenol (0.94 g, 10 mmol) was reacted with NaOH (0.400 g, 10 mmol) in water (100 mL) to form a clear aqueous solution. Then the aqueous solution was added dropwise to the cyanuric chloride solution. After stirring at 0 °C for 8 h, the mixture was poured into water (100 mL) to form a white precipitate. The white precipitate was filtered and washed with water and ethanol. The product was purified by recrystallization with hexane to give a white solid. Yield: 80 %.

¹H NMR (300 MHz, CDCl₃) δ (ppm): 7.43–7.36 (m, 4H), 7.28 (dd, J = 7.8, 1.4 Hz, 2H), 7.17–7.11 (m, 4H).

Synthesis of 4,6,10,12,16,18,19,20,21-nonaaza-5,11,17-triphenoxy-2,8,14-trithiacalix[3]arene

2,4-dichloro-6-phenoxy-1,3,5-triazine (8) (2000 mg, 8.26 mmol) was dissolved in dry THF and the solution was purged with nitrogen for 10 minute. The NaSH (860 mg, 15.30 mmol) was added to the solution and the reaction was occurred at 60 °C for 72 hour. After completion of reaction, the solution was dissolved in a mixture of dichloromethane and distilled water. The organic fraction was then washed with water, dried with K₂CO₃, filtered and solvent evaporated to dryness. The crude production was purified over a silica column with *n*-heptane/ethyl acetate (v/v: 3/1) as eluent to obtain a light yellow powder as the pure product. Yield: 18 %.

¹H NMR (300 MHz, acetone-d₆) δ (ppm): 7.46-7.35 (m, 2H), 7.34-7.23 (d, 1H), 7.22-7.12 (m, 2H). ¹³C NMR (75 MHz, acetone-d₆) δ (ppm): 181, 171, 152, 130, 127, 122.

Synthesis of 1,3,5-tris(4-bromophenyl)benzene

4-Bromoacetophenone (5 g, 25.13 mmol), 0.25mL of H₂SO₄ (conc.) and K₂S₂O₇ (6.6 g, 26.14 mmol) were heated at 180 °C for 16 h under a nitrogen atmosphere. The resulting crude solid was cooled to room temperature and refluxed in 25mL of dry ethanol (EtOH) for 1 h and then cooled to room temperature. The solution was filtered and the resulting solid was refluxed in 25mL of H₂O to give a pale yellow solid that was then filtered. The crude product was dried under vacuum giving 7.5 g of dried product, which was recrystallized from CHCl₃ (yield 55%).

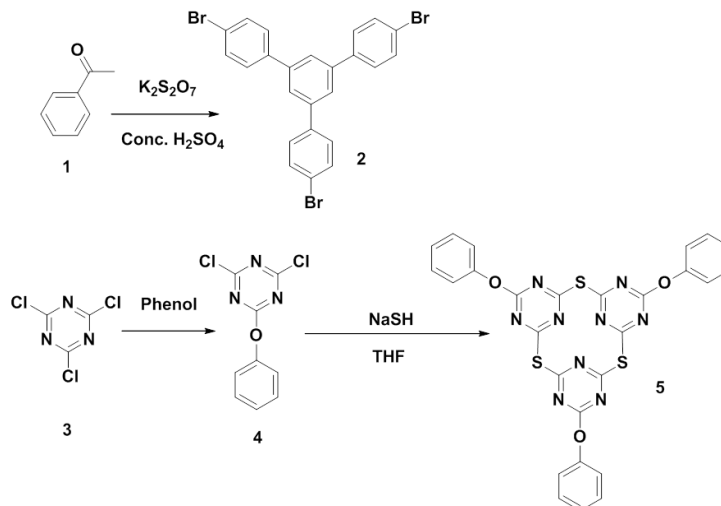
¹H NMR (300MHz, CDCl₃) δ (ppm): 7.53 (d, 6H), 7.60 (d, 6H), 7.68 (s, 3H)

RESULTS AND DISCUSSION

The 4,6,10,12,16,18,19,20,21-Nonaaza-5,11,17-triphenoxy-2,8,14-trithiacalix[3]arene was synthesized from cyanuric chloride with the yield

of 20%. In the first step, 2,4-dichloro-6-phenoxy-1,3,5-triazine was synthesized from phenol in the presence of NaOH, the yield of this reaction was obtained around 80%. Then, the 2,4-dichloro-6-phenoxy-1,3,5-triazine was continuously reacted with NaSH to obtain 4,6,10,12,16,18,19,20,21-

Nonaaza-5,11,17-triphenoxy-2,8,14-trithiacalix[3]arene. In the other hand, 1,3,5-tris(4-bromophenyl)benzene (5) was synthesized from 4-acetophenol with a yield of 55%. The synthesis of these compounds was presented in Scheme 1.



Scheme 1. The synthesis of thiacalix[3]triazine and 1,3,5-tris(4-bromophenyl)benzene compounds

The chemical structure of 4,6,10,12,16,18,19,20,21-nonaaza-5,11,17-triphenoxy-2,8,14-trithiacalix[3]arene monomer was elucidated by ¹H NMR (Figure 1). ¹H NMR spectrum of 4,6,10,12,16,18,19,20,21-Nonaaza-5,11,17-triphenoxy-2,8,14-trithiacalix[3]arene showed the signals attributed to the phenyl protons

in range of 7.22 to 7.5 ppm with those corresponding all protons of phenyl rings. The integration of proton signal is also reasonable with structure of 4,6,10,12,16,18,19,20,21-nonaaza-5,11,17-triphenoxy-2,8,14-trithiacalix[3]arene monomer.

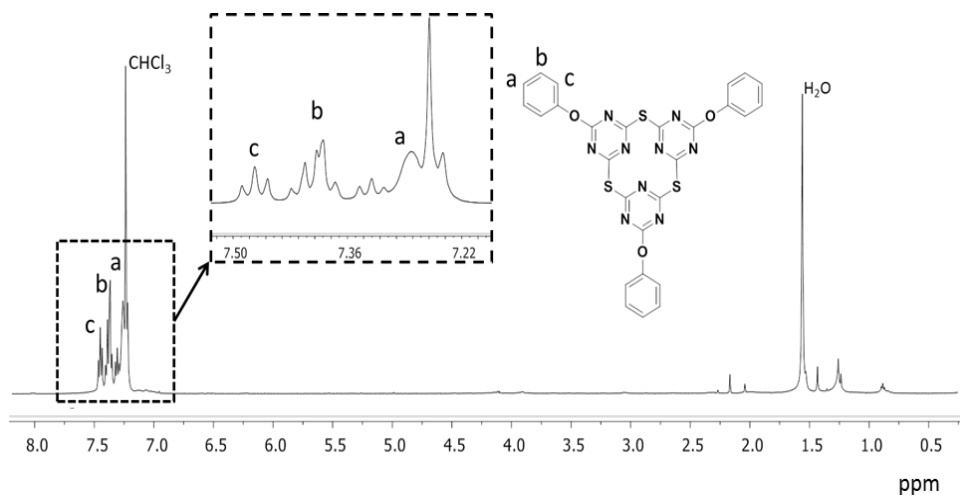


Figure 1. ¹H NMR of 4,6,10,12,16,18,19,20,21-nonaaza-5,11,17-triphenoxy-2,8,14-trithiacalix[3]arene

The chemical structure of 1,3,5-tris(4-bromophenyl)benzene compound monomer was also elucidated by ^1H NMR (Figure 2). ^1H NMR spectrum of 1,3,5-tris(4-bromophenyl)benzene showed the signals attributed to the phenyl protons

in range of 7.5 to 7.8 ppm with those corresponding all protons of phenyl rings. The integration of proton signal was also reasonable with structure of 1,3,5-tris(4-bromophenyl)benzene.

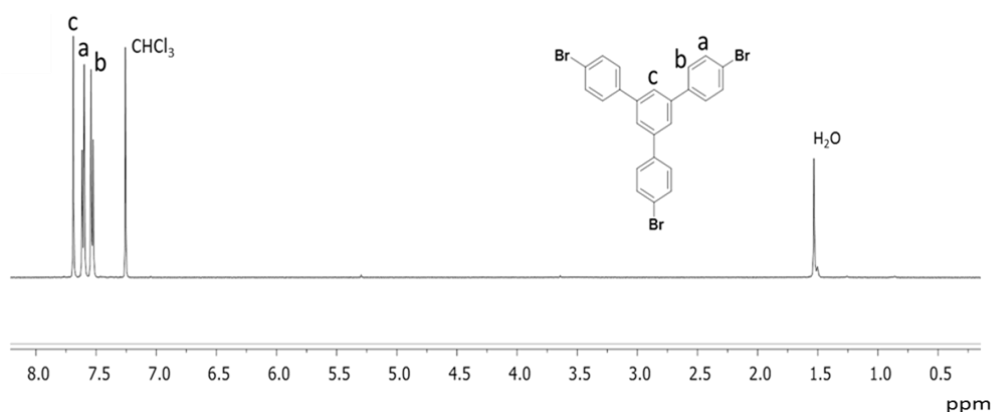


Figure 2. ^1H NMR of 1,3,5-tris(4-bromophenyl)benzene

In order to explore the optical properties of 4,6,10,12,16,18,19,20,21-nonaaza-5,11,17-triphenoxy-2,8,14-trithiacalix[3]arene and 1,3,5-tris(4-bromophenyl)benzene related to fluorescence switching caused by an anion association with core structure, a solution of compounds such as 4,6,10,12,16,18,19,20,21-Nonaaza-5,11,17-triphenoxy-2,8,14-trithiacalix[3]arene or 1,3,5-tris(4-bromophenyl)benzene were prepared in THF ($C_M = 0.1$ M) in the present of tetra-*n*-ethylammonium hydrogen carbonate. Solution of 10^{-3} M of the tetra-*n*-ethylammonium hydrogen carbonate was prepared with the host stock solution to remain a constant host concentration throughout the anion association experiment. In the case of 1,3,5-tris(4-bromophenyl)benzene fluorescence property of polymer was not change with an addition of tetra-*n*-ethylammonium hydrogen carbonate. However, in the case of 4,6,10,12,16,18,19,20,21-nonaaza-5,11,17-triphenoxy-2,8,14-trithiacalix[3]arene, an addition of 10^{-4} mmol of tetra-*n*-ethylammonium hydrogen carbonate in the solution of polymer resulted in a decrease of the fluorescence intensity,

dropping of 11% of the initial value. This phenomenon is referred to fluorescence quenching, which is caused by effective energy transfer from p,6,10,12,16,18,19,20,21-nonaaza-5,11,17-triphenoxy-2,8,14-trithiacalix[3]arene moieties to the anion complex formed of thiacalix[3]triazine core and $[\text{HCO}_3^-]$. In addition, the emergence of absorbance peak around 310 nm that corresponding to the anion complex formed by thiacalix[3]triazine core and $[\text{HCO}_3^-]$. We also investigated the influence of tetra-*n*-ethylammonium hydrogen carbonate concentration on the decreasing of fluorescence intensity. As seen in Fig. 3, when we increased the concentration of tetra-*n*-ethylammonium hydrogen carbonate in the polymer solution, the fluorescence quenching of compounds was reached and limited at 60% comparing with the initial value.

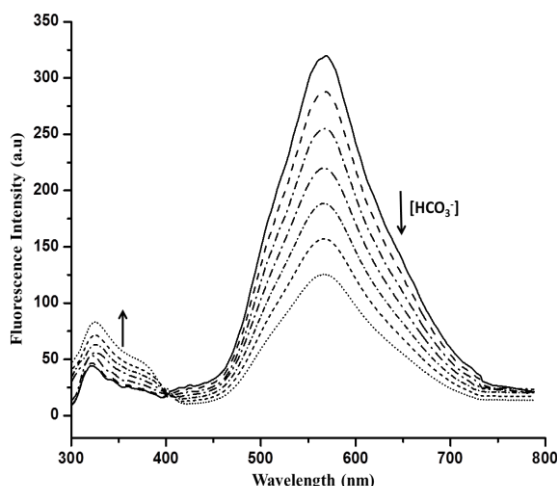


Figure 3. Emission spectra of 4,6,10,12,16,18,19,20,21-Nonaaza-5,11,17-triphenoxy-2,8,14-trithiacalix[3]arene in THF ($C_M = 0.1$ M) in the presence of tetra-*n*-ethylammonium hydrogen carbonate

CONCLUSION

In this research, we have demonstrated the synthesis of 4,6,10,12,16,18,19,20,21-nonaaza-5,11,17-triphenoxy-2,8,14-trithiacalix[3]arene and 1,3,5-tris(4-bromophenyl)benzene. The synthesized compound was fully characterized to determine the chemical structure of these compounds. Moreover, the 4,6,10,12,16,18,19,20,21-nonaaza-5,11,17-triphenoxy-2,8,14-trithiacalix[3]arene or 1,3,5-tris(4-bromophenyl)benzene exhibited the anion association resulted the fluorescence quenching which could be useful for chemsensor application to detect the toxic anions in the environment.

Acknowledgements: This research was supported by The Department of Science and Technology (DOST) – Ho Chi Minh City [QĐ774/QĐ-SHKCN]

Tổng hợp và đánh giá hợp chất hữu cơ thiacalix[3]triazine và 1,3,5-tris(4-bromophenyl)benzene cho ứng dụng làm cảm biến hóa học

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TÓM TẮT

Hợp chất thiacalix[3]triazines và 1,3,5-tris(4-bromophenyl)benzene được tổng hợp qua các phản ứng đơn giản và được phân tích nhằm xác định cấu trúc hóa học của những hợp chất. Hợp chất thiacalix[3]triazines được phân tích qua phổ cộng hưởng từ proton và phổ cộng hưởng từ carbon và được xác định đúng với cấu trúc hóa học. Thêm vào

đó hợp chất thiacalix[3]triazines thể hiện bước sóng hấp thụ tối đa tại 560 nm và bước sóng cao nhất tại 720 nm tương ứng với độ rộng vùng cấm của thiacalix[3]triazines là 1.72 eV. Hợp chất thiacalix[3]triazines với cấu trúc vòng ba cùng với nguyên tố S là cấu nối trong cấu trúc vòng giữa các vòng aryl, hợp chất này đã cho thấy khả năng tương tác với anion và có thể hữu ích trong việc ứng dụng làm cảm biến hóa học.

Keywords: thiacalix[3]triazines, 1,3,5-tris(4-bromophenyl)benzene, cảm biến hóa học, heteroaryl, conjugated polymers

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