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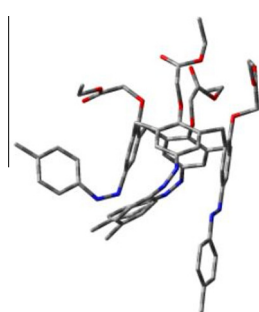
## The synthesis and characterization of azocalix[4]arene based chemosensors and investigation of their properties

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### HIGHLIGHTS

- In this study, azocalix[4]arene tetraester derivatives (**4a–f**) were synthesized.
- Their thermal decomposition analysis was performed by means of TG, DTA and DTG.
- Azocalix[4]arene derivatives have showed a good selectivity toward Hg<sup>2+</sup> and Hg<sup>+</sup> ions.

### GRAPHICAL ABSTRACT



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### ABSTRACT

In the present study, azocalix[4]arenes were prepared by linking 4-methoxy, 4-methyl, 4-ethyl, 4-chloro, 4-bromo and 4-nitroaniline to calix[4]arene through a diazo-coupling reaction. A new family of azocalix[4]arene tetraester derivatives, (**4a–f**), have been prepared with the incorporation of ethyl ester units to azocalix[4]arene. Characterization of the synthesized azocalix[4]arenes was carried using elemental analyses, UV–vis, FT-IR and <sup>1</sup>H NMR spectroscopic techniques. The effect of varying pH levels and solvent types on the absorption ability of azocalix[n]arenes substituted with electron-donating and electron-withdrawing groups was examined. Thermal decomposition of azocalix[4]arene derivatives (**4a–f**) was investigated by means of thermogravimetry (TG), differential thermogravimetry (DTG) and differential thermal analysis (DTA) analyses. In conclusion of the examination of the extraction we found a selectivity characteristic of these compounds toward Ag<sup>+</sup>, Hg<sup>+</sup> and Hg<sup>2+</sup> cations.

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### Introduction

Calix[4]arenes play an important role in supramolecular chemistry as molecular scaffolds for elaborating sophisticated hosts [1–4]. Functional groups are introduced into the existing calix[n]arene framework by a functionalized method either through the “lower rim” (the oxygen-position of the phenolic moieties) or the “upper rim” (the *p*-position of the aromatic nuclei) [5].

Literature surveys show that the majority of the existing studies have not only focused on the thermal behavior but also concentrated on functionalization [6].

A variety of functional groups have been regio- and stereospecifically introduced on the hydroxy groups of calix[4]arenes as recognition sites by linking moieties through etherification. However, the transformation causes the location of the functional groups to be apart from the calix skeleton [7,8]. This situation makes it difficult for guests to be affected by the steric effects of the calix skeleton and/or to interact with substituents which are present on it (e.g., with residual hydroxy groups or linking hetero atoms). This

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issue may be addressed by cleaving the aryl–oxygen bonds, thereby replacing the hydroxy groups with different functional groups. However, such a transformation is quite difficult for calix[4]arenes because of their steric and electronic environment in proximity to the *lower rim* [9,10], in addition to the poor nucleofugacity of the phenolic hydroxy group.

Calix[*n*]arenes are extensively used in selective extraction of metals, nuclear waste treatment, catalysis, complexation of fullerenes and neutral molecules. Their synthesis procedure, in addition to their physical characterization techniques (in terms of their physical properties such as melting point, solubility and acid dissociation constant, pKa) are complicated [1,2]. The high melting points of these compounds necessitate a careful investigation of their thermal behavior. Thermal analysis methods have been extensively applied in the field of polymers, solid/liquid interface, carbohydrate chemistry, minerals, energetic materials, pharmaceutical and biochemistry [11–13].

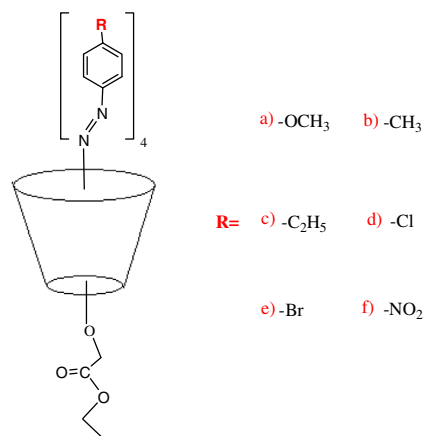
Thermogravimetric analysis is a valuable tool for the determination of inclusion behavior of calix[*n*]arenes with guest molecules such as toluene, xylene, chloroform, acetone, methanol and alkyl ammonium [14,15]. Increasing temperature leads to loss of small functional groups from the main calix[*n*]arene body. As the temperature increases, the chain length of the leaving functional groups increases. Calix[*n*]arenes are good antioxidants of polyolefins such as polypropylene, and polyethylene [16–18]. It is reported that, more than 20,000 ton of phenolic antioxidants were consumed during 1983 for the stabilization of plastics in USA alone. This data clearly reveals the importance of antioxidants in terms of the polymer industry [19]. The present study is concerned with the synthesis of azocalix[*n*]arenes and investigation of their thermal decomposition kinetics.

Schatz et al. studied solid state inclusion of various organic solvent molecules in *p-tert*-butylcalix[*n*]arene [15]. After their study, synthesis and characterization of *p-tert*-butylcalix[6]arene ammonium cation complexes have been reported. A similar study was also reported by Radius et al., who prepared calix[4]arene-supported iron(III) complexes [20].

As reported in [21–23], secondary and tertiary amine complexes of calixresorcinarenes are formed in a solution with a complementary fit with the calix cavity size. Calixresorcinarene forms complexes with amines with a stoichiometry ratio of 1:2 in the solid-state. There are several variations of decomposition structures of azocalixarenes/calixarenes, or azocalixarene metal complexes as shown by X-ray crystallography. These structures present variable positions of various metal cations, some of which fill the cavity by interacting with the electron clouds and the others by forming hydrogen bonds with phenolic oxygens.

Recently, synthesis and theoretical investigation of calix[4]arene derivatives and their complexes, polymeric calix[*n*]arene derivatives and azocalix[*n*]arenes have been reported by our research group [24]. We examined the selective extraction of Fe<sup>3+</sup> ion from aqueous phase into the organic phase as well as the liquid–liquid extraction of transition metal ions using diazo-coupled calix[*n*]arenes. However, there is still an important need for systems those can explain color changes with ionic or molecular interactions [25–27].

In this study, we have mainly looked into the development of a new class of chromogenic azocalix[4]arene chemosensors. This work focuses on thermal behavior and decomposition of six diazo-coupled azo substituted calix[4]arenes (**4a–f**) (Scheme 1). There are an insufficient number of reports on the thermal decomposition analysis of azocalix[4]arene-based compounds so far. Hence, this study has been a research effort to fill this gap in the academic literature.



Scheme 1. Diazo-coupled azocalix[4]arene tetraester derivatives (**4a–f**).

## Experimental

All reagents and solvents were purchased from Merck, Sigma–Aldrich and Carlo-Erba Company and used without further purification. *p-tert*-Butylcalix[4]arene, calix[4]arene, *p*-substitute phenylazocalix[4]arenes (**3a–f**) 25,26,27,28-tetrakis(ethoxycarbonylmethoxy)-5,11,17,23-tetrakis[(4-methoxyphenyl)azo]calix[4]arene (**4a**), 25,26,27,28-tetrakis(ethoxycarbonylmethoxy)-5,11,17,23-tetrakis[(4-methylphenyl)azo]calix[4]arene (**4b**), 25,26,27,28-tetrakis(ethoxycarbonylmethoxy)-5,11,17,23-tetrakis[(4-ethylphenyl)azo]calix[4]arene (**4c**), 25,26,27,28-tetrakis(ethoxycarbonylmethoxy)-5,11,17,23-tetrakis[(4-chlorophenyl)azo]calix[4]arene (**4d**), 25,26,27,28-tetrakis(ethoxycarbonylmethoxy)-5,11,17,23-tetrakis[(4-bromophenyl)azo]calix[4]arene (**4e**) and 25,26,27,28-tetrakis(ethoxycarbonylmethoxy)-5,11,17,23-tetrakis[(4-nitrophenyl)azo]calix[4]arene (**4f**) were synthesized as described in previously reported methods [28–34].

## Instrumental

Melting points of analyzed compounds were measured using an Electrothermal IA9100 digital melting point apparatus in capillaries sealed under nitrogen and they were used without correction. <sup>1</sup>H NMR spectra were referenced to tetramethylsilane (TMS) at 0.00 ppm as the internal standard solution and were recorded on a Bruker 400 MHz spectrometer at room temperature (25 ± 1 °C). IR spectra were recorded by a Mattson 1000 FTIR spectrometer using KBr pellets. UV–vis spectra were obtained by a Shimadzu 1601 UV–Visible recording spectrophotometer. The elemental analyses were performed in the Laboratories of TUBITAK (The Scientific and Technological Research Council of Turkey).

Crystallization solvent was remained in some of the analytical samples and affected the elemental analysis results. In such cases, best fits between the analytical values and appropriate fractional increments of solvents were used.

TG, DTG and DTA curves of analyzed compounds were obtained simultaneously by using a Shimadzu DTG-60H thermal analyzer. The measurements were realized in platinum crucible and flowing air atmosphere (25 mL min<sup>-1</sup>). Potential applications of the calyx[*n*]arenes, such as selective extraction, azo dyes component and antioxidant properties, are realized in air atmosphere. So we chose air atmosphere. The analyzed temperature range was 25–850 °C. The heating rate was set to 10 °C min<sup>-1</sup> and the sample masses were between 3–5 mg. Highly sintered α-Al<sub>2</sub>O<sub>3</sub> was used as the reference material. Before carrying out the experiments, it is essential to calibrate the balance for buoyancy effects for the

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