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RESEARCH STUDY ON AZO CALIXARENES AND THEIR APPLICATION

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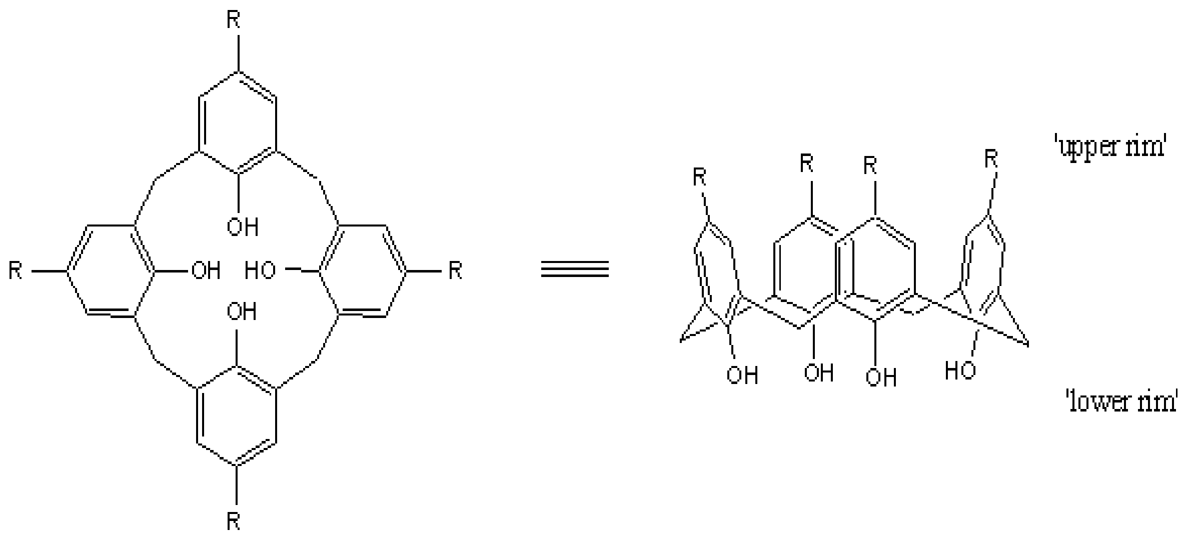
INTRODUCTION

Baeyer pioneered the chemistry of calixarenes although he was unable to determine its structure. In 1902, Baekland made phenol formaldehyde resins a commercial success under the trade name Bakelite. In these resins phenol and formaldehyde are exhaustively condensed with each other to form heavily cross-linked polymers. The first attempt to control the reaction was made by Zinke and Ziegler in 1942. They employed para substituted phenols which inhibits crosslinking and should result in a linear polymer with formaldehyde.

The original Zinke's procedure was several step processes that involved (a) treating a para substituted phenol with aqueous formaldehyde and NaOH at 50-55^{0}C for 45 h., (b) heating the reaction mixture at 110-120^{0}C for 2 h, during which time the water evaporated to leave fibrous solid, (c) acidifying the residue, and finally (d) suspending the resin in linseed oil and heating at 220^{0}C for several hours. The products of this method are high melting and insoluble which have been assigned as cyclic tertramer by Zinke. This method was modified by introduction of one step procedure known as the 'Munch procedure' or the 'Petrolite procedure in which a mixture of para substituted phenol, paraformaldehyde and little amount of an alkali was refluxed in xylene for 4 h or more**.** Later the researcher replaced linseed oil by diphenyl ether or biphenyl eutectic.

The world calixarene was coined by C. D. Gutsche in the late 1970s led to a renewed interest in this field and his naming such products calix[n]arene because of the resemblance between the shapes of calixarene, the cyclic tetramers and a type of Greek vase. Here arene indicating the presence of aromatic rings and a bracketed number positioned between calix and arene indicates the number of phenolic units linked to each other by methylene bridges to form the cavity of the molecule. Calixarenes are the most targeted molecule in the field of Supramolecular Chemistry. Calixarene provides three-dimensional versatile platform on which variety of functional groups is attached and a wide family of molecular receptors endowed with recognition properties toward ions and neutral molecules are obtained. The derivatives of functionalized calixarenes can encapsulate all most all metals present in the periodic table. It has been shown from literature survey that the most studied class of periodic table is alkali and alkaline earth metals. The cavity of calixarene enables it to encapsulate the in coming metal ion within the cavity without any functionalization. Researchers have introduced a variety of functional groups like ester, ether, amide etc. to enhance the binding properties. There were number of synthetic methodologies for the synthesis of theses macrocyclic compounds via condensation of phenols and formaldehyde.



Calix[4]arene [Fig. 1]

SYNTHETIC MODIFICATIONS ON CALIXARENE PLATFORM

The structure of calixarene is the most favorable basic frame to construct variety of supramolecular assemblies. The alterations of parent calixarene have been modified by number of ways such as,

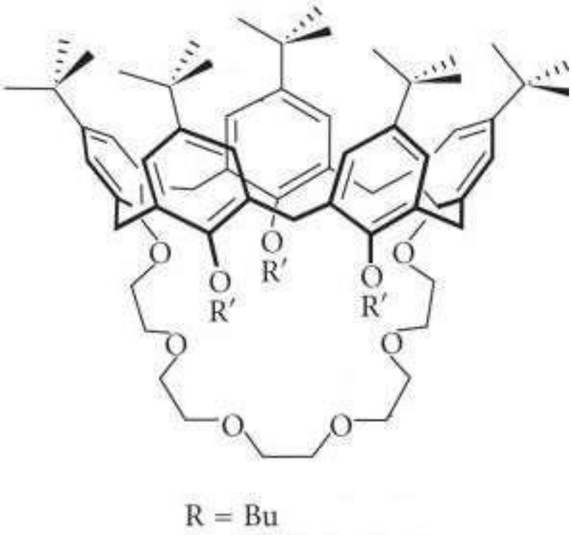
1) Lower rim functionalization,
2) Modifications of Methylene bridges,
3) Upper rim functionalization.

1) Lower rim functionalization

The phenolic hydroxy groups at the lower rim of calixarenes represent an excellent reactive site for the introduction of functional groups which modify the shape and the binding properties of these molecules.

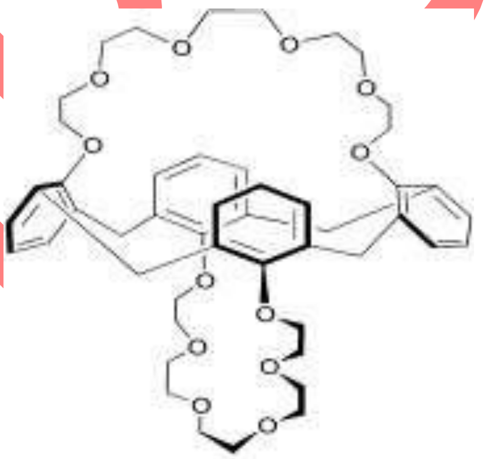
Reaction of calixarene **[Fig. 1]** with a strong base in dimethylformamide in the presence of alkylating reagent usually leads to complete O-alkylation of calix[n]arenes which can be further modified by re-esterification, acylation, tosylation and substitution by various nucleophiles.

Another path in which the narrow rim of calix [4] arene can be modified to bridged derivatives with difunctional reagents. These bridged calixarene derivatives could be achieved by direct O-alkylation with ditosylates (under the conditions used for selective di-O-functionalization), which is frequently used for the preparation of various 1,2- and 1,3-calix[4]crowns **[Fig. 2]**.



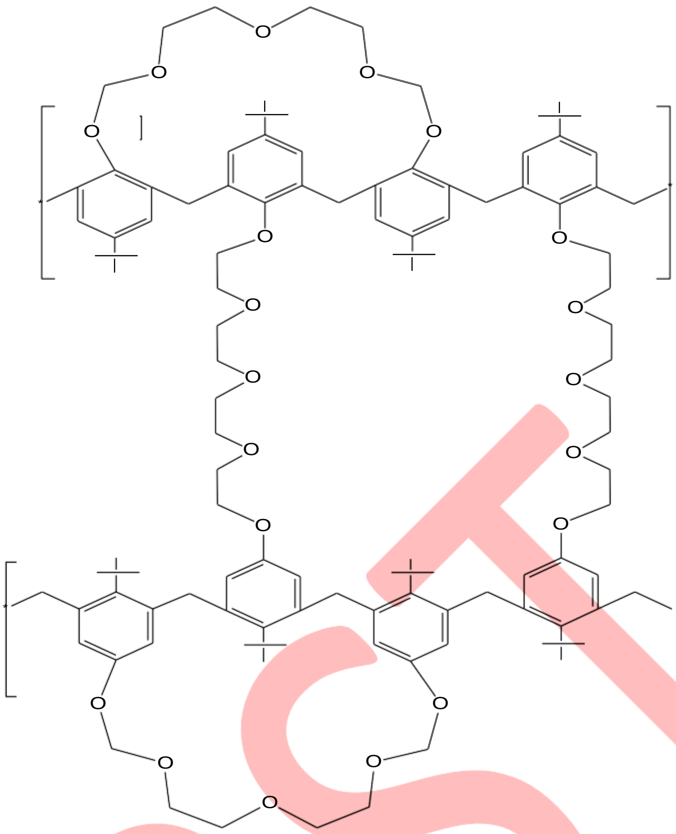
1,3-calix[4]crown [Fig. 2]

These bridged dihydroxy derivatives can be further alkylated by monofunctional or difunctional reagents (introduction of the second bridge) leading to the exhaustively alkylated products, which in the second case are doubly-bridged calixarenes (calix[4]arene-bis crown) **[Fig. 3]**. Depending on the reaction conditions the products could be obtained in the cone or 1,3-alternate conformation



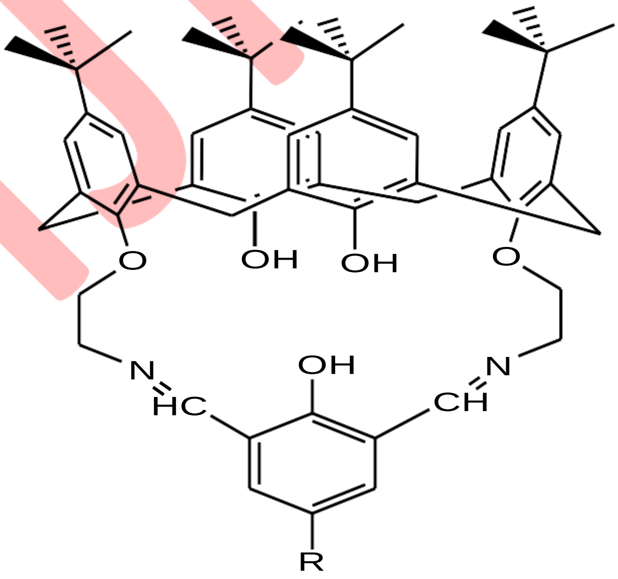
Calix[4]arene-bis crown [Fig. 3]

On the other hand the bridging of the calix[4]arenes extended to bis-calixarene by difunctional reagents via two functional groups already attached to the phenolic oxygens at 1,2- or 1,3-positions by O-alkylation leading to intermolecularly bridged products **[Fig. 4]**.



Bis-calix[4crown ether [Fig. 4]

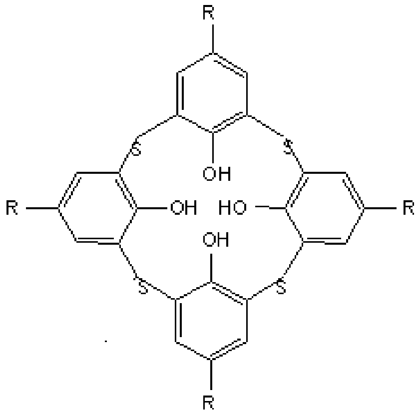
The field of O-alkylated calixarene then directed towards new trends that is Schiff base calixarene. The lower rim calixarene Schiff base has been reported by Wan et al. in 2002. They showed the use of lower rim amine derivative for the synthesis of Schiff base calixarene. **[Fig. 5]**.



Schiff base calix[4]arene [Fig. 5]

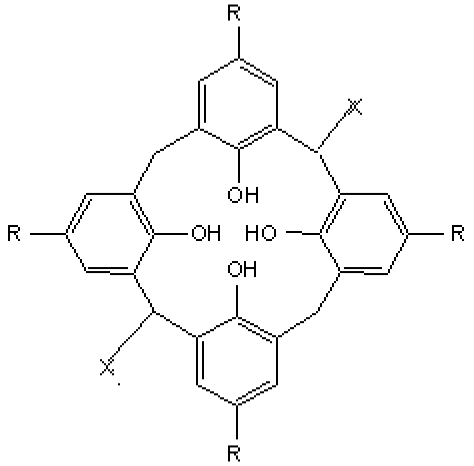
2) Modification of methylene bridges

Apart form upper rim and lower rim, calixarene possesses methylene bridges which is also a synthetically active site. The modification of methylene bridges with hetero atom such as sulfur is the recent trends in calixarene chemistry **[Fig. 6]**. Moreover, Biali et al. have reported different substitution on methylene bridge **[Fig. 7]**.



Where, R=t-Bu

Methylene bridge modified by sulfur [Fig. 6]



where, X=Me, Et, t-Bu, iso-Pr and R=Me

Methylene bridge modified by various groups [Fig. 7]

3) Upper rim functionalization

The tert-butyl groups of p-tert-butyl-calix[n]arene can be easily removed by trans-alkylation with $AlCl_3$ and toluene, which is used as a solvent and as an acceptor, where phenol is also used to increase the rate of the reaction, possibly because steric reasons. It may be more efficient than the calixarene in generating the H^+ necessary to initiate the reaction. The free para-positions of phenolic units of this resulting substrate, calix[4]arene**,** have been further functionalized via electrophilic substitution or rearrangements. Such as nitration, chloromethylation, formylation, aminomethylation and acylation of calixarene and their coupling with diazonium salts have been described. Substituents introduced at the upper rim by electrophilic substitution can be replaced or modified by further reactions.

Nitration

Yong et al. have carried out the nitration of calix[4]arene and calix[6]arene using nitrogen dioxide. Nitro group of calixarene can be reduced by catalytic hydrogenation, by hydrazine or by Sn(II) yielding tetra amino calixarene. This tetra amino calixarene on acylation has led to various amides and ureas, while the reaction of tetra amino calixarene with aldehyde produces the Schiff-bases.

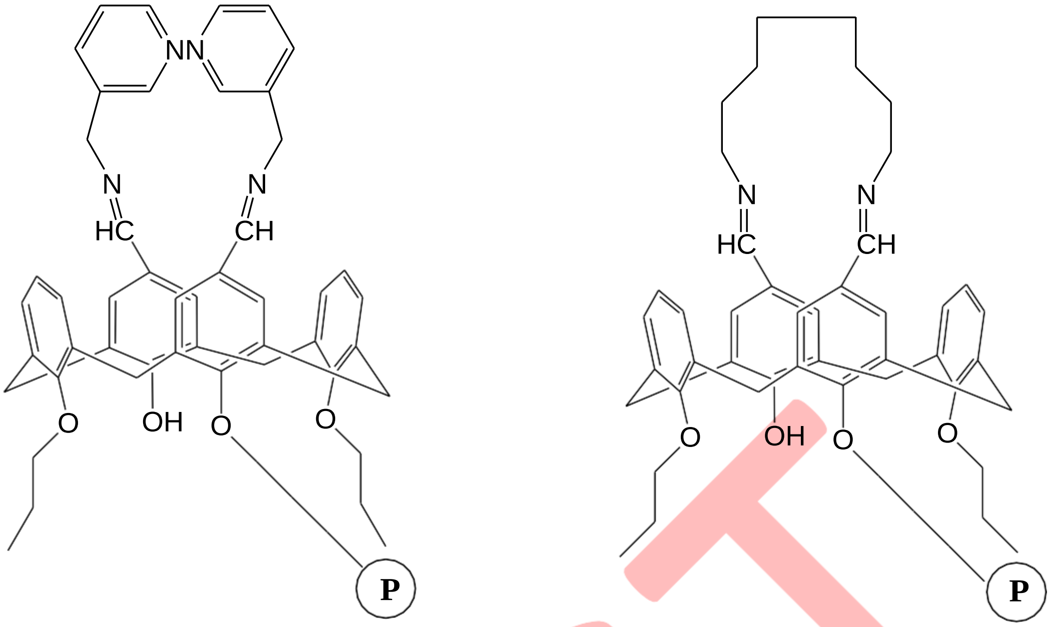
Chloromethylation

In 1992, Arduini et al. have first used chloromethylated calix[4]arene were reduced or alkylated to yield p-methyl and p-ethyl compounds respectively. Moreover, the reaction of these chloromethylated calixarene derivatives with aromatic compounds in the presence of BF_3 gives p-arylmethyl calixarenes.

Formylation

The study of formyl calixaerne was started in nineteen centuries. These formyl calixarene derivatives can oxydized to the corresponding carboxylic groups. p-Stilbene derivatives are obtained from tetraaldehyde by Wittig-Horner reaction.

The work on formylated calicarene has been extended by synthesized 5,17-diformyl-25,27-dipropoxy-26,28-dihydroxycalix[4]arene which was obtained by formylation of de-tert-butylated calix[4]arene. Karakucuk have been reported new polymer supported receptors in which the upper rims of calixarene were modified by introduction of imine linkage. These receptors have been synthesized from 5,17-diformyl-25,27-dipropoxy-26,28-dihydroxycalix[4]arene and 3-amino-methylpyidine, 1,8-diaminooctane in the presence of $MgSO_4$ in methanol medium, which have been appended to a polymeric resin by treatment with Merrifield resin through a nucleophilic substitution reaction. In this case the polymer support brought down the solubility of ionophores and hence these receptors have been studied for binding abilities towards transition metal cations by solid-liquid extraction method **[Fig. 8]**.



A **B**

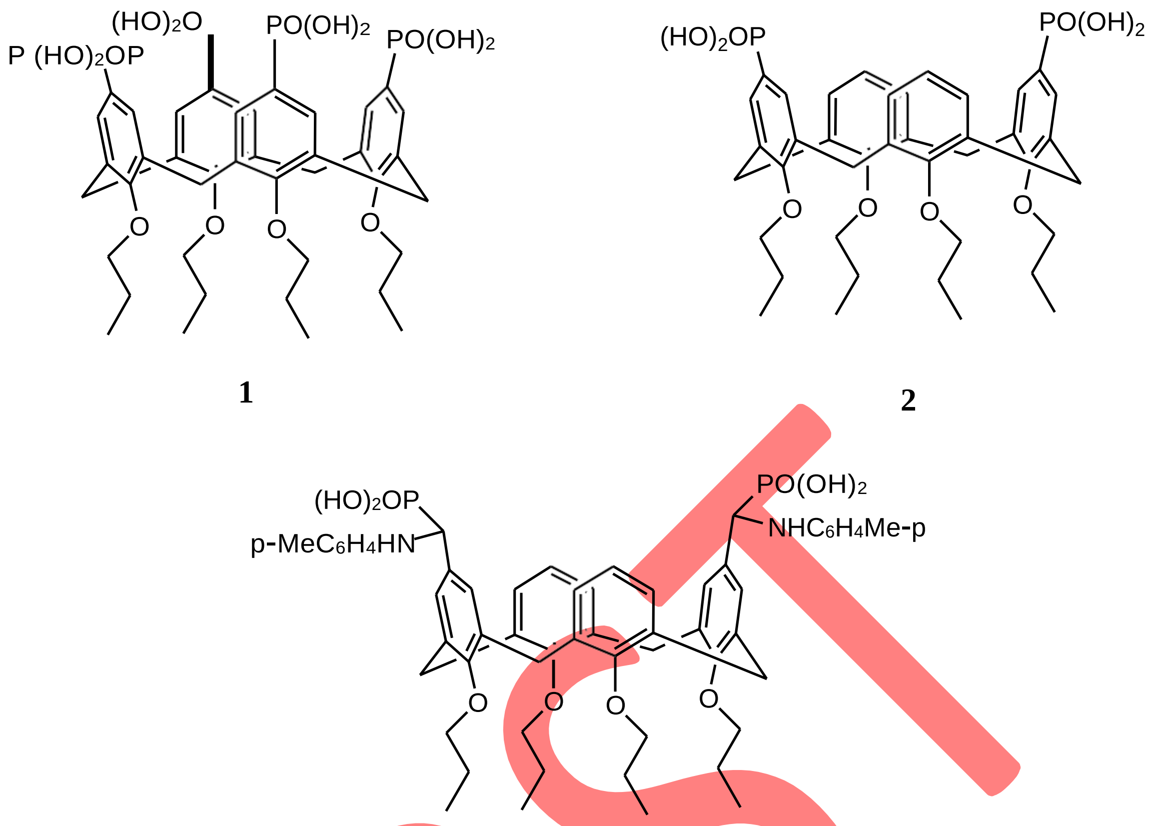
Where, P = Polymer

Upper rim substituted calix[4]arene with imine linkage [Fig. 8]

Aminomethylation

Aminomethyl group in calixarene has been introduced by Mannich reaction with secondary amine. This derivative can be substituted by cyano nucleophile to yield cyanomethylated derivative. The hydrolysis of this derivative produces carboxy derivative of calixarene and reduction of cyanomethyl derivative leads the amine derivative of calixarene.

This approach has been enlarged to organometallic complexes. The organometallic complexes of rhodium have been reported by Martin et al.. In 2003, Kalchenko et al. have reported the complexation properties of calix[4]arenephosphorous with herbicides such as 2,4-dichlorophenoxyacetic acid and atrazine in water by means of reserve phase HPLC method [**Fig. 9**]. They concluded that the herbicides were encapsulated due to the hydrophobic cavity of macrocycles, their π-π* interactions and electrostatic forces between calix[4]arenephosphorous and herbicides.



1

2

3

Calix[4]arenephosphorous derivative
[Fig. 9]

Acylation

The recent trend involves the acylation of calixarene followed by coupling with diazonium salt. This azo group having remarkable properties in calixarene world has been described below.

RESEARCH METHODOLOGY

It has been well documented that most of the functional groups are unable to be incorporate into calixarene frameworks by direct condensation. Literature survey shows that majority of studies were concentrated on the lower rim functionalization, with only few concentrating on the upper rim of calixarenes. Among the upper functionalized methods, Gutsche et al. have reported the allyl group introduction by Claisen rearrangement route, and other several research groups reported that the aryl azo groups can be incorporated by direct diazonium coupling method. Nomura et al. reported that the UV-vis spectra of azo-calix[4]arene have been changed upon the binding of metal ions or amines. While azo coupling reaction of calix[4]arenes were studied by Morita et al. The azo-calixarenes were extensively studied by

Deligöz et al. A verity of chromogenic substitutions was combined with calixarene such as nitrophenylazo, nitrophenol, indoaniline, indophenol, azophenol and investigated for their chromogenic properties towards Na^+, K^+, Cs^+, Ca^+, Ni^{2+}, Hg^{2+}, Cr^{2+} and UO^{2+}. Shinkai et al. have synthesized calix[4]arene with a 4-(4-nitrophenyl)azophenol unit and observed Li^+ sensitivity for the azo ionophore. Whereas Toth et al. have reported the Na^+ selectivity of related azophenol derivatives of calixarene. There are also reports on encapsulation of anions by azo-calixarenes such as Cl^-.

Till today all the synthesized chromogenic azo-calixarenes have been utilized in the field of host guest chemistry. It is also well known that the azo group is one of the most useful functional groups in the field of commercial dyes. To the best of our literature knowledge, there are no such reports on the use of azo-calixarenes as a coloring agent in the textile industries. In our present work, our efforts have been diverted towards direct commercial application base synthesis of macrocycles such as calixarenes. We have synthesized seven new azo-calixarenes in order to evaluate their coloring properties in the textile industries. The synthesis was achieved by reacting different substituted amino sulphonic acid and different derivatives of aniline with tetrahydroxycalix[4]arene at 0-5^{0}C temperature using various solvent systems. The choice of coupler has been made by checking their properties as a dyeing agent on protein fiber such as wool, leather and synthetic polyamide fiber such as nylon. All these synthesis of azo-calix[4]arene derivatives were also carried out without using the newly developed microwave method.

CONCLUSION

In our present study, the water insoluble azo-calixarenes bearing nitro and acetamido functional groups were examined for their printing properties on plastics. It has been concluded that apart for their thermal and solvent stabilities calix-pigments are not appropriate as plastic pigments due to their low strength on plastic sheets. However as described in chapter 4 the azo-calixarene are showing excellent results as acid dyes for their application as coloring agent on polyamide fibers such as nylon. Moreover, we have also noted that these pigments are showing dull shed on test specimens compare to commercially available pigments. But the thermal stabilities and solvent stabilities are good enough. So, it is possible to increase the strength by adjusting the structure of azo-calixarene by adding more chromophoric groups such as nitro or methoxy.

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