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# *p*-Nitrophenylazo Calix[4]arenes, Synthesis, Monolayers and NLO-properties

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**The mono, bis, tris and tetrakis (*p*-nitrophenyl)azo calix[4]arenes (1, 2, 3 and 4) with NLO properties are synthesized by the diazo-coupling of calix[4]arene with *p*-nitrophenyl diazonium. HRS measurements at 1064 nm indicate that (*p*-nitrophenyl)azo calix[4]arenes have higher second-order hyperpolarizability β values than the corresponding reference compound 4-(4-nitrophenylazo)-2,6-dimethylphenol, without red shift of the charge transfer band. The bis and tris (*p*-nitrophenyl)azo calix[4]arenes (2, 3) without hydrophobic alkyl chains can form stable Langmuri monolayers at the air/water interface because of arene π–π stacking.**

*Keywords*: Calix[4]arene; NLO; Second-order hyperpolarizability; Monolayer

## INTRODUCTION

Organic compounds with second-order non-linear optical (NLO) properties have various potential in the development of materials for applications such as frequency doubling and optical switching [1,2]. Traditional organic NLO materials are organic molecules that contain electron-donating and electron-accepting groups connected via a conjugated π system, i.e. so called D–π–A structure. Generally, the second-order non-linear hyperpolarizability β of a molecule increases with increasing length of the conjugated π system and increasing strength of the donor and acceptor [3]. Unfortunately, an increase in the β value is accompanied by a red shift in the absorption spectra due to a larger π-conjugated length and/or stronger donor and acceptor substituents, i.e. there is a trade-off between nonlinearity and transparency [4].

Calix[4]arenes are cyclophanes that consist of four phenol moieties connected by methylene bridges [5]. Upon functionalization, up to four D–π–A units can be introduced within a single molecule. If calix[4]arene exists in the cone conformation, non-conjugated D–π–A units are oriented at nearly the same direction. Therefore, this system has the increased NLO activity and is not accompanied with an unfavourable shift of absorption to longer wavelengths. Some calix[4]arene derivatives with NLO properties have been reported [6–10]. Especially, Reinhoudt et al. introduced strong electron-withdrawing moieties, such as (nitro)ethenyl, (tricyano)-ethenyl, (4-nitrophenyl)ethenyl, thiobarbituric acid group at the upper rim of calix[4]arene to form preorganized chromophore molecules and demonstrated that they have both high second-order β value and good transparency [11]. Therefore, calix[4]arene system with NLO active moieties is a promising organic chromophore molecule. Recently, our interest also lies in the synthesis of calixarenes with NLO properties and their possible applications. For this purpose, the mono, bis, tris and tetrakis (*p*-nitrophenyl)azo calix[4]arenes (**1**, **2**, **3** and **4**) (Scheme.1) have been prepared in our laboratory through the diazo-coupling of calix[4]arene with *p*-nitrophenyl diazonium. HRS measurements indicated that they have higher second-order hyperpolarizability β values than the corresponding reference compound 4-(4-nitrophenylazo)-2,6-dimethylphenol, without red shift of the charge transfer band. Moreover, we found the bis and tris (*p*-nitrophenyl)azo calix[4]arenes (**2**, **3**), although without longer alkyl chains, can form stable

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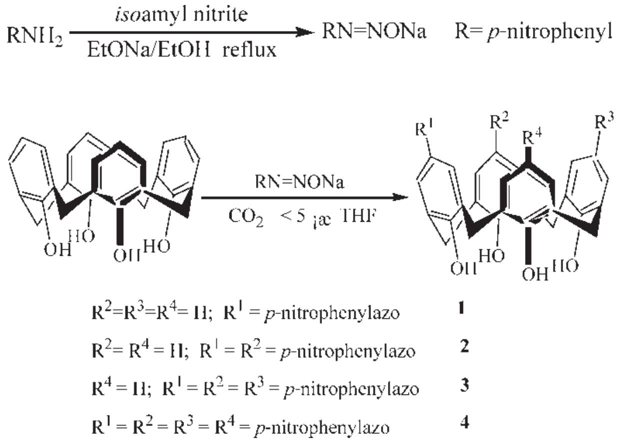

SCHEME 1 Synthesis of *p*-nitrophenylazo-substituted calix[4]arenes.

Langmuir monolayers at the air/water interface because of arene π–π stacking.

## RESULTS AND DISCUSSION

### Synthesis

The synthetic methods of azo calix[4]arenes reported were usually carried out by the diazo-coupling reaction of calix[4]arene with diazonium fluoroborates or diazoniums chlorides prepared from the diazotization reaction of substituted anilines with sodium nitrite in concentrated HCl [12–14]. In these preparations, tetrakis(arylazo)-substituted calix[4]-arenes were always obtained as a main product because of an auto-accelerative effect. In the present method, arylamines were diazotized with *iso*-amyl nitrite in EtONa/EtOH and the diazo-coupling reactions were carried out in the presence of carbon dioxide gas in non-aqueous solution at 0–5°C [15]. When calix[4]arene and different molar ratio of *p*-nitroaniline were used, corresponding mono-, bis-, tris- or tetrakis *p*-nitrophenylazo calix[4]arenes were produced in yields of 61.9, 17.2, 33.5 and 52.0%, respectively. All the *p*-nitrophenylazo calix[4]arenes are characterized by $^{1}$H NMR, $^{13}$C NMR, MS, IR and elemental analysis. In the $^{1}$H NMR spectra, the methylene protons of $ArCH_2Ar$ of azocalix[4]arenes always appeared as broad signals at room temperature. When $^{1}$H NMR spectra were measured at −20°C,the broad signals became sharper and a splitting pattern appeared. The chemical shift values and splitting pattern of the methylene protons at low-temperature are summarized in Table I. The tetrakis(*p*-nitrophenyl)azo calix[4]arene **4** displays one pair of doublets because it is symmetrical compound. The mono(*p*-nitrophenyl)azo calix[4]-arene **1** displays two pairs of doublets with a ratio of 1:1. The bis(*p*-nitrophenyl)azo calix[4]arenes **2** displays three pairs of doublets with a ratio of 1:2:1, and three peaks of the methylene carbons appear in range of 31.5–33.5 ppm in the $^{13}$C NMR. Therefore compounds **2** is 5, 11-disubstituted (*proximal*) isomer. The higher statistical probability at the *proximal* positions than to the *distal* positions in the diazo-coupling reactions may be the main reason for producing *proximal* isomer. The $^{1}$H NMR splitting pattern of the methylene hydrogens at low-temperature and chemical shift values (within the range of 31.3–33.6 ppm) of the methylene carbons.also indicate that these (*p*-nitrophenyl)azo calix[4]arenes have a cone conformation [16,17].

TABLE I $^{1}$H NMR δ values and splitting pattern for methylene hydrogens of (*p*-nitrophenyl)azo calix[4]arenes (600 MHz, −20°C)

| Compounds | δ(ppm) | splitting pattern* |
|---|---|---|
| mono- (**1**) | 4.34, 4.29, 3.71, 3.59 | two pair of doublets (1:1) |
| 5,11-di-(**2**) | 4.41, 4.39, 4.37, 3.84, 3.71, 3.59 | three pair of doublets (1:2:1) |
| tri- (**3**) | 4.55, 4.49, 3.64, 3.49 | two pair of doublets (1:1) |
| tetra- (**4**) | 5.08, 3.90 | one pair of doublets |

* All coupling constants are about 13.8 Hz.

### Second Order Hyperpolarizability β and the Absorption Maximum Values

Hyper-Rayleigh scattering (HRS) measurements [18] for (*p*-nitrophenyl)azo calix[4]arenes **1**, **2**, **3** and **4** and the corresponding reference compound 4-(4-nitrophenylazo)-2,6-dimethylphenol **5** were performed with a fundamental wavelength of 1064 nm in THF. The second order hyperpolarizability β and the absorption maximum of the charge-transfer band ($\lambda_{CT}$) are summarized in Table II.

It can be seen from Table II that the compounds **1**, **2**, **3** and **4** have higher second order hyperpolarizability β values than the corresponding reference compound **5**, and a favourable blue-shift of the charge transfer band can be observed. Based on the cone conformation, two D–π–A moieties of **2** do not behave as totally independent NLO unit, so β is 1.6 times the value of the reference compound **5** with only one D–π–A unit. It is surprising that **2** with two D–π–A moieties have a higher β value than **4** and **3** with four or three D–π–A moieties. The steric

TABLE II Second order hyperpolarizability β (in THF, at 1064 nm), charge-transfer band $\lambda_{CT}$ and melting points for (*p*-nitrophenyl)azo calix[4]arenes

| Compound | β ($\times 10^{-30}$ esu) | $\lambda_{CT}$ (nm) | m.p.(°C) |
|---|---|---|---|
| **4** | 296.6 | 374 | >320 |
| **3** | 275.2 | 378 | >320 |
| **2** | 302.6 | 382 | >320 |
| **1** | 233.1 | 378 | 302–304 |
| **5** | 186.7 | 387 | |

congestion at the upper rim area of calix[4]arene due to the bulky *p*-nitrophenyl-(*E*)-azo units may make the cone conformation flat, i.e. the average angles of the D−π−A moieties with the dipole axis of **4** or **3** are much larger than those of **1** and **2**. It is also notable that the melting points of *p*-nitrophenylazo calix[4]-arenes excess 300°C, so they have good thermal stability. Therefore, the calix[4]arene system with NLO active moieties may be useful in resolving the non-linearity-transparency-thermal stability tradeoff.

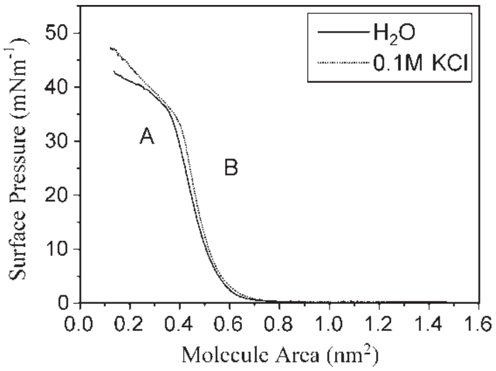

FIGURE 2 π−A isotherms of the monolayers of compound **3** (A) on the surfaces of pure water, (B) on 0.1 M KCl aqueous solution.

## Monolayers of *p*-Nitrophenylazo calix[4]arenes at the Air/Water Interface

The orientation of the molecules is necessary for NLO materials having higher second order hyper-polarizability β values, which can be achieved with the Langmuir-Bloggett technique. We studied the spreading behaviour of *p*-nitrophenylazo calix[4]-arenes at the air/water interface. It was found that the compounds **2** and **3** can formed stable monolayers at the air/water interface although they have no hydrophobic alkyl chains. But compound **1** can not form monolayers at the air/water interface, and compound **4** was not studied because of its very low solubility in organic solvent Figs. 1 and 2 show the π−A isotherms of the **2** and **3** monolayers on pure water and 0.1 M KCl aqueous subphase On pure water, it is observed that both **2** and **3** can form stable monolayers and **2** (about 50 m Nm$^{-1}$) has higher collapse pressure than **3** (about 38 m Nm$^{-1}$). The limiting molecular area of **2** and **3** are 0.43 and 0.48 nm$^2$/molecule, respectively. According to the proposal of Coleman [19], calix[4]arene can take two kinds of molecular orientations at the air−water interface, i.e. the parallel orientation and the perpendicular orientation. The limiting molecular area of the latter is less than 0.65 nm$^2$/molecule. Therefore both **2** and **3** may mainly take an orientation perpendicular to the air-water interface. The spreading behaviours of **2** and **3** on 0.1 M KCl aqueous subphase have also been studied. KCl in the aqueous subphase does not cause much difference in the shape of their π−A isotherms, only the limiting molecular area of **2** expands slight outward. This indicates that the interaction of the monolayers and KCl is very weak. Up to now, all calixarene molecules

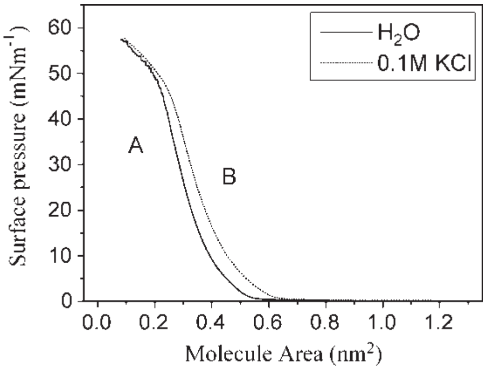

FIGURE 1 π−A isotherms of the monolayers of compound **2** (A) on the surfaces of pure water, (B) on 0.1 M KCl aqueous solution.

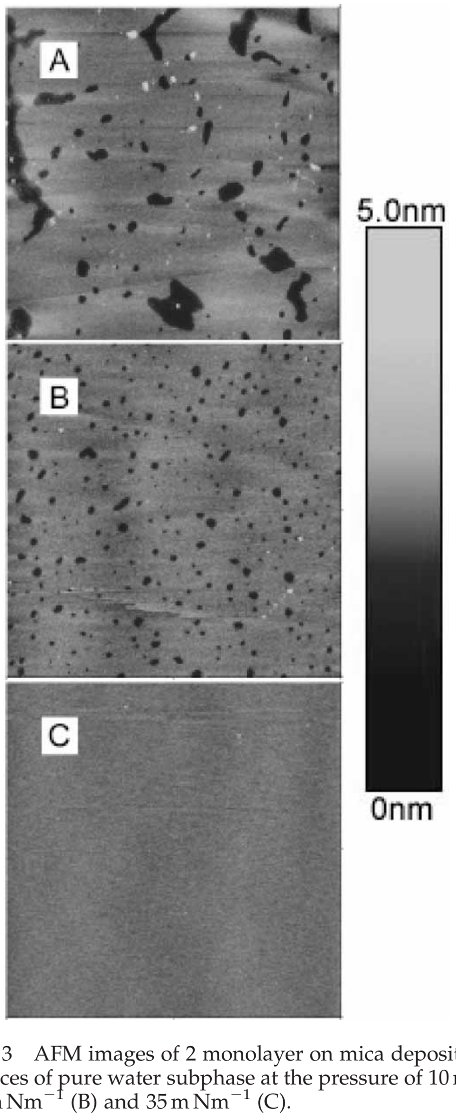

FIGURE 3 AFM images of 2 monolayer on mica deposited from the surfaces of pure water subphase at the pressure of 10 m Mm$^{-1}$ (A), 20 m Nm$^{-1}$ (B) and 35 m Nm$^{-1}$ (C).

forming stable monolayers have hydrophobic long alkyl chains or *t*-butyl groups [6,20–26], while compounds **2** and **3** have not hydrophobic alkyl chains. Why can form they stable monolayers? Atwood has reported the bipolar amphiphilic calixarene without hydrophobic alkyl chains can self-organized to form two-dimensional bilayers in aqueous solution due to areneπ–πstacking interaction [27]. The reason of *p*-nitrophenylazo calix[4]-arenes **2** and **3** monolayers can also ascribed to arene π–π stacking interaction.

Figs. 3 and 4 show the AFM images of monolayers of compound **2** on mica deposited from the surfaces of pure water and 0.1 M KCl aqueous subphase, respectively. It is obvious that the AFM images on mica from two kinds of subphases are almost similar and the arrangement of the compounds at the air/water becomes closed with the pressure increase.

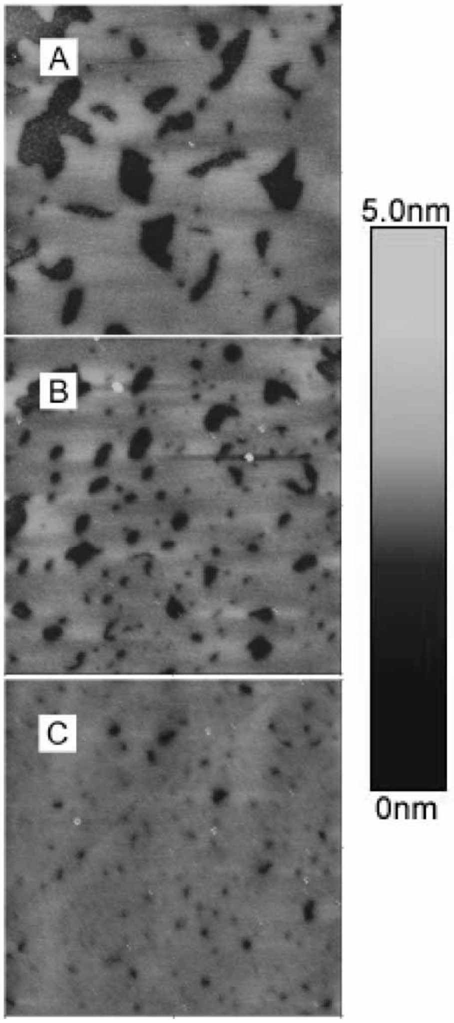

FIGURE 4 AFM images of **2** monolayer on mica deposited from the surfaces of a 0.1 M KCl solution subphase at the pressure of 10 m Mm$^{-1}$ (A), 20 m Nm$^{-1}$ (B) and 35 m Nm$^{-1}$(C).

## CONCLUSION

The *p*-nitrophenylazo calix[4]arenes **1a**, **1b**, **1c** and **1d** have been synthesized by the diazo-coupling of calix[4]arene with *p*-nitrophenyl diazonium.produced from the *p*-nitroaniline with *iso*-amyl nitrite in EtONa/EtOH solution. HRS measurements indicate that they have higher second-order hyperpolarizability β values than the corresponding reference compound 4-(4-nitrophenylazo)-2,6-dimethylphenol, and no red shift of the charge transfer band has been observed. Therefore, calix[4]-arenes with NLO-active moieties are promising and interesting building blocks for designing organic NLO materials with both highβvalue and good transparency. In addition, *p*-nitrophenylazo calix[4]-arene **2** and **3** without longer alkyl chains can also form the stable monolayer at air/water. Therefore it is possible to assemble novel organic ordered film with NLO properties.

## EXPERIMENTAL

Melting points were determined on a Yanaco micro melting point apparatus. Samples for elemental analysis were dried in vacuo at 60°C. Elemental analyses were carried out using Perkin–Elmer 240C. $^1$H NMR and $^{13}$C NMR were recorded on Inova 600. MS spectra were recorded by electrospray mass spectrometer (LCQ, Finnigan) in negative mode. IR spectra were recorded on Bruker IFS 66v (Germany). UV spectra were measured on Jasco V-530 ultraviolet-visible spectrophotometer. The AFM images were taken by a digital instruments Nanoscope IIIa. All the surface pressure-area isotherms were determined on a KSV(mini trough) film balance. Preparative column chromatography separations were performed on G60 silica gel, while precoated silica gel plates (GF$_{254}$) were used for analytical TLC. All the solvents were purified by standard procedures.

### Preparation of (*p*-Nitrophenyl)azo calix[4]arenes

A solution of *p*-nitroaniline (6.0 mmol) in anhydrous ethanol (60 ml) was slowly added to a solution of NaOEt (120 mmol) in anhydrous ethanol (60 ml) under stirring, and then *iso*-amyl nitrite (0.6 ml, 6.6 mmol) was added. The mixture was refluxed for 5 h. After cooling, the precipitate of diazotate salt was filtered and dissolved in 30 ml of anhydrous ethanol. A solution of a given amount of calix[4]-arene in anhydrous THF (80 ml) was added to the solution of diazotate salt at 0–5°C, and carbon dioxide gas was passed through the mixture in order to adjust to appropriate pH value. After continuous stirring for 2–8 h, water (200 ml) was added, the red-brown precipitate was collected by filtration, which was separated by column chromatography to give (*p*-nitrophenyl)azo calix[4]arenes.

### *5-Mono-[(4-nitrophenyl)azo]-25, 26, 27, 28-tetrahydroxycalix[4]arene (1)*

m.p.:302–304°C; Yield: 52.0%; $R_f = 0.30$ ($CHCl_3$: petroleum ether = 3 : 1). MS(ESIMS): $m/z = 572.7$ ($[M - H]^-$, calc. 572.3). IR(KBr): $\nu = 1591.8$ (N=N), 1341.8($NO_2$). $^1H$ NMR (600 MHz, $CDCl_3$, 25°C): $\delta =$ 10.20 (bs, 4H, -OH), 8.33 (d, $J = 9.0$ Hz, 2H,ArH in the 4-nitrophenyl moiety), 7.92 (d, 2H, ArH in the 4-nitrophenyl moiety),7.74 (s, 2H, ArH in the azo phenol moiety), 7.15 (d, $J = 7.8$ Hz, 2H, ArH in the phenol moiety), 7.09 (d, $J = 7.8$ Hz, 2H, ArH in the phenol moiety), 7.05 (d, $J = 7.8$ Hz, 2H, ArH in the phenol moiety), 6.77 (t, $J = 7.8$ Hz, 2H, ArH in the phenol moiety), 6.73 (t, $J = 7.8$ Hz, 1H, ArH in the phenol moiety), 4.29 (bs, 4H, $ArCH_2Ar$), 3.69 and 3.57 (bs, 4H, $ArCH_2Ar$). $^{13}C$ NMR (600 MHz, $CDCl_3$): $\delta = 32.1$, 32.7($ArCH_2Ar$),118.8, 120.1, 121.8, 124.9, 126.3, 128.7, 129.3, 130.4, 131.1, 132.3, 140.9, 141.5, 150.5, 151.3, 153.8(aromatic C). Anal. Calcd. for $C_{34}H_{27}$ $N_3O_6$: C, 71.19; H, 4.74; N, 7.33. Found: C, 70.85; H, 5.12; N, 7.17.

### *5,11-Bis-[(4-nitrophenyl)azo]-25, 26, 27, 28-tetrahydroxycalix[4]arene (2)*

m.p.: >320°C; Yield: 33.5%; $R_f = 0.75$ ($CHCl_3$: $C_5H_5N$ = 10 : 1). MS(ESIMS): $m/z = 721.4$ ($[M - H]^-$, calcd. 721.2). IR(KBr): $\nu = 1592.8$ (N=N), 1341.5($NO_2$). $^1H$ NMR (600 MHz, pyridine-$d_5$, 25°C): $\delta = 8.26$ (d, $J = 9.0$ Hz, 4H, ArH in the 4-nitrophenyl moiety), 8.20(s,2H,ArH in the azo phenol moiety), 7.91(d, $J = 9.0$ Hz, 4H, ArH in the 4-nitrophenyl moiety), 7.80(s,2H,ArH in the azo phenol moiety), 7.06(d, $J = 7.8$ Hz, 2H, ArH in the phenol moiety), 6.99(d, $J = 7.8$ Hz, 2H, ArH in the phenol moiety),6.63 (t, $J = 7.8$ Hz, 2H, ArH in the phenol moiety), 4.30 (bs, 4H, $ArCH_2Ar$), 3.59 (bs, 4H, $ArCH_2Ar$). $^{13}C$ NMR (600 MHz, pyridine-$d_5$): $\delta =$ 31.9, 32.5, 33.4($ArCH_2Ar$),119.1, 120.3, 122.5, 125.4, 126.5, 128.9, 129.4, 130.5, 131.5, 132.6, 140.6, 141.2, 145.5, 147.6, 150.4, 152.2, 153.4, 154.9(aromatic C). Anal. Calcd. for $C_{40}H_{30}$ $N_6O_8$: C, 66.48; H, 4.18; N, 11.63. Found: C, 66.12; H, 4.32; N, 11.35.

### *5, 11, 17-tris-[(4-Nitrophenyl)azo]-25, 26, 27, 28-tetrahydroxycalix[4]arene (3)*

m.p.: > 320°C(dec); Yield: 17.2%; $R_f = 0.25$ ($CHCl_3$: $C_5H_5N$ = 10 : 1). MS(ESIMS): $m/z = 870.8$ ($[M - H]^-$, calc. 870.4). IR(KBr): $\nu = 1598.2$ (N=N), 1341.5($NO_2$). $^1H$ NMR (600 MHz, pyridine-$d_5$, 25°C): $\delta = 8.35$(d, $J = 9.0$Hz, 2H, ArH in the 4-nitrophenyl moiety), 8.29(s, 2H, ArH in the azo phenol moiety), 8.24 (d, $J = 9.0$ Hz, 4H, ArH in the 4-nitrophenyl moiety), 8.07(s, 2H, ArH in the azo phenol moiety), 8.01(d, $J = 9.0$ Hz, 2H, ArH in the 4-nitrophenyl moiety), 7.97 (s, 2H, ArH in the azo phenol moiety), 7.83(d, $J = 9.0$ Hz, 4H, ArH in the 4-nitrophenyl moiety),7.22(d, $J = 7.8$ Hz, 2H, ArH in the phenol moiety), 6.78(t, $J = 7.8$ Hz, 1H, ArH in the phenol moiety), 4.56 (bs, 4H, $ArCH_2Ar$), 3.64 (bs, 4H, $ArCH_2Ar$). $^{13}C$ NMR (600 MHz, pyridine-$d_5$): $\delta =$ 31.7, 32.5($ArCH_2Ar$),118.9, 120.8, 122.4, 125.6, 126.4, 128.7, 130.4, 131.7, 132.5, 140.5, 141.1, 145.3, 147.8, 151.5, 152.1, 153.9, 154.7, 155.1(aromatic C). Anal. Calcd. for $C_{46}H_{33}$ $N_9O_{10}$: C, 63.37; H, 3.82; N, 14.46. Found: C, 63.03; H, 3.94; N, 14.75.

### *5,11,17,23-tetrakis-[(4-Nitrophenyl)azo]-25,26,27,28-tetrahydroxy calix[4]arene (4)*

m.p.: >320°C(dec); Yield: 61.9%; $R_f = 0.30$ ($CH_3COOC_2H_5$: $CH_3COCH_3$ = 10 : 1). MS(ESIMS): $m/z = 1019.7$ ($[M - H]^-$, calc. 1019.3). IR(KBr): $\nu =$ 1591.2 (N=N), 1340.3($NO_2$). $^1H$ NMR (600 MHz, pyridine-$d_5$, 25°C): $\delta = 8.23$ (d, $J = 9.0$ Hz, 8H,ArH in the 4-nitrophenyl moiety), 8.19 (s, 8H, ArH in the azo phenol moiety), 7.81 (d, $J = 9.0$ Hz, 8H, ArH in the 4-nitrophenyl moiety), 5.08 (bs, 4H, $ArCH_2Ar$), 3.88 (bs, 4H, $ArCH_2Ar$). $^{13}C$ NMR (600 MHz, pyridine-$d_5$): $\delta = 32.4$ ($ArCH_2Ar$),118.7, 124.1, 129.1, 130.3, 141.2, 145.6, 152.3, 154.4 (aromatic C). Anal. Calcd. for $C_{52}H_{36}$ $N_{12}O_{12}$: C, 61.18; H, 3.55; N, 16.46. Found: C, 60.78; H, 3.79; N, 16.10.

## HRS Measurements

HRS measurements experiments were performed with a fundamental wavelength of 1064 nm in THF. The HRS experimental setup used here is similar to that of Clays *et al.* [18]. The light source was a Q-switched Nd:YAG laser (Continuum, Surelite II) with a pulse duration of 8 ns full width half maximum (FWHM), operating at a repetition rate of 5 Hz at a wavelength of 1064 nm. The pump laser beam was focused into a sample cell by a cylindrical lens system. The light was collected at 90° to the incident beam and was measured with a photomultiplier tube. The signal was recorded with a digital oscilloscope (Tektronix TDS 3032). Wavelength discrimination was accomplished by means of a 3 nm bandwidth interference filter centered at 532 nm.

## Surface Pressure-area Isotherms Experiments

Surface pressure-area isotherms ($\pi$–A isotherms) were measured on KSV 5000 (mini trough). The temperature was kept at 20 ± 0.2°C. Monolayers were formed by spreading 36 μl $5 \times 10^{-4}$ M chloroform / DMF solution of **2** and **3** onto the surface of deionized water (purified by Milli-Q system, (18 MΩ, pH ~ 5.6) or a 0.1 M KCl aqueous subphase, respectively. The π–A isotherms were measured three times at a barrier speed of 4 mm/min and were found reproducible.

## AFM Images of Monolayer Films

When the surface pressure raised to the desired magnitude during compression, the barriers were stopped and the monolayer films of azocalixarenes were transferred onto freshly cleaved mica for AFM observations.(transfer ration was almost unity).

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