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Synthesis and anion binding of 2-arylazo-*meso*-octamethylcalix[4]pyrroles

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2-Arylazo-5,5,10,10,15,15,20,20-octamethylcalix[4]pyrroles (azo-OMCPs) have been synthesised by the reaction of calix[4]pyrrole with aryldiazonium chloride in 15–45% yields. The solution-state binding studies of the synthesised hosts were investigated by absorption spectroscopy and ^{1}H NMR in DMSO and $CDCl_3$, respectively. These receptors, appended with electron-donating and electron-withdrawing groups, displayed enhanced affinity and selectivity for fluoride anion. Well-defined colour change in the visible region of the spectrum was observed upon addition of fluoride ion in DMSO solution of azo-OMCPs. Detailed NMR studies in $CDCl_3$ revealed that azo-OMCPs with nitro and chloro groups have higher binding affinity for fluoride ion.

Keywords: functional calix[4]pyrroles; anion binding; neutral receptor; UV–vis spectroscopy; azo coupling

Introduction

The synthesis of anion receptors possessing high affinity and adequate selectivity for various targeted substrates is an ongoing challenge in the area of supramolecular chemistry due to their important roles in biological systems. Here, materials capable of reversible anion-induced colour changes are particularly attractive as they require little or no instrumentation for practical uses (*1–4*). Various attempts have been made to develop the fluoride ion sensors due to its diverse uses in different biological, medical and environmental processes (*5–7*).

Meso-octamethylcalix[4]pyrrole (OMCP) is an appealing synthetic target due to its easy synthesis and ability to bind anions (*8*) and neutral substrates (*9*, *10*) mainly through multiple hydrogen-bonding interactions. OMCP and related porphyrinogens are macrocyclic species formed by cyclocondensation of pyrrole with ketones under different acidic conditions (*11*, *12*). Over the past two decades, studies on calixpyrroles have proliferated to synthesise and characterise various functionalised derivatives for understanding, improving and tuning the binding affinity and selectivity of different anions (*13–36*). More recently, OMCP-based supramolecular assemblies formed by $\pi-\pi$ charge-transfer interaction have been used for selective sensing of amino acids and amine in an unbuffered water-containing media (*37, 38*). Functionalisation at β-pyrrolic position of calixpyrrole is especially valuable because such systems can be assembled by either acid-prompted condensation of substituted pyrrole with the appropriate ketone or direct condensation approach.

In an elegant work, Azenbacher and co-workers have explored the electrophilic aromatic substitution reactions as a useful motif to develop chromophoric calix[4]pyrroles (*39–41*) and related compounds (*42–44*) capable to bind with various anions including halides, acetate and phosphate even in the presence of competing media such as water and electrolytes.

Herein, we report the synthesis of a series of azo-OMCPs, functionalised at the β-position and their role in binding of different anions under different conditions.

Results and discussion

The condensation of acetone and pyrrole catalyzed by Amberlyst-15™ in dichloromethane gave **OMCP** (**1**) and **NC-OMCP** (**2**) in 83 and 14% yield, respectively (*45*). The reaction of **1** with aryldiazonium chloride gave 2-arylazo-*meso*-octamethylcalix[4]pyrroles **4a**–**4f** in quantitative yield (Scheme 1). Indeed, one of the azo-sensor **4f** has been synthesised by the reaction of **1** with *p*-nitrophenyldiazonium tetrafluoroborate in the presence of triethylamine in 9% yield (*41*). However, improved yield of **4f** was obtained with freshly prepared diazonium chloride. The anion-binding events shown by **4f** provoked us to develop a series of new azo-sensors. The synthesised azo-OMCPs **4a**–**4f** are characterised by IR, UV–vis, ^{1}H NMR, ^{13}C NMR and ESI-MS techniques. For example, compound **4a**

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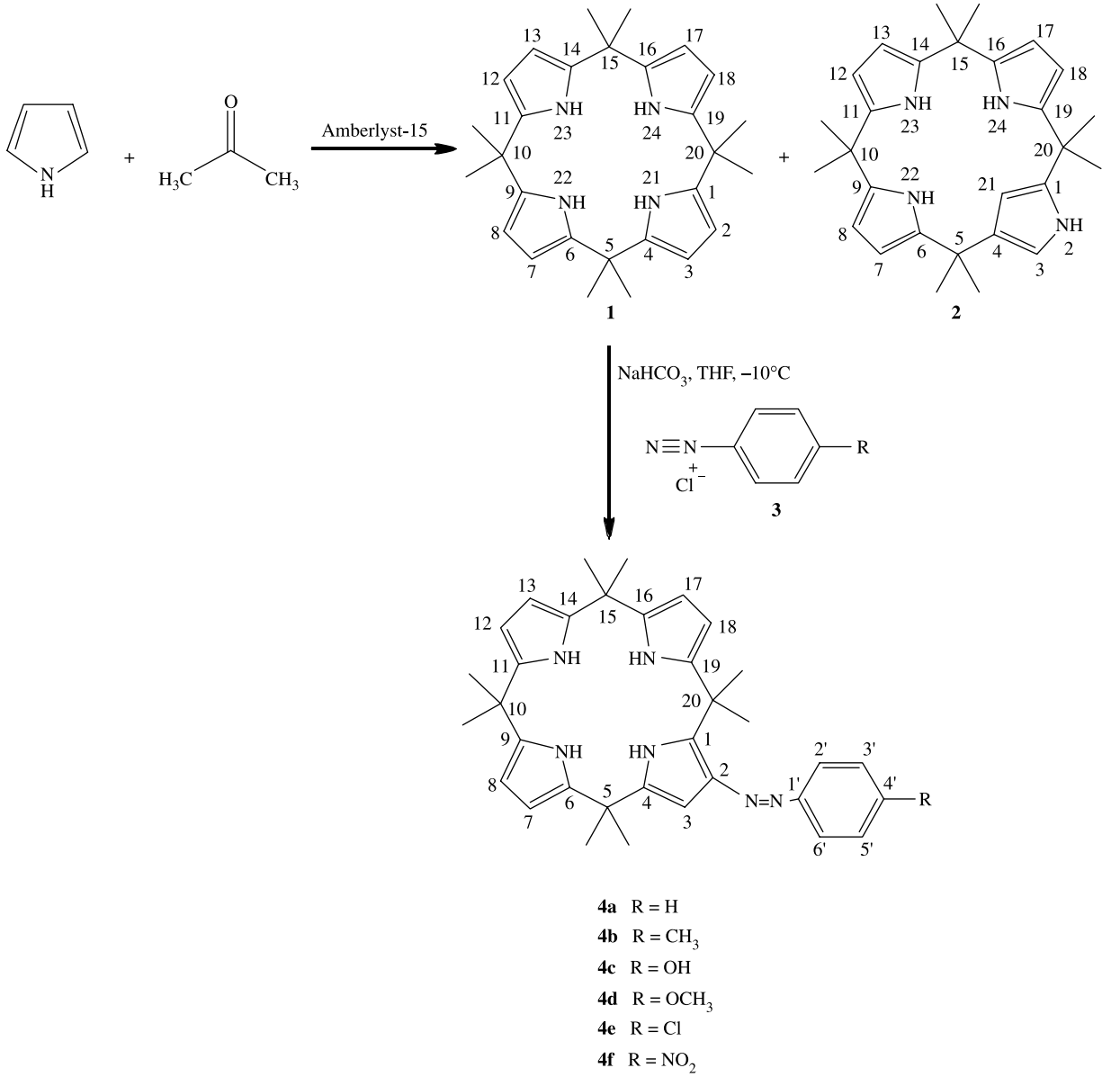
showed characteristic vibrations of pyrrolic-NH (3441 cm^{-1}) and —N=N— group (1598 cm^{-1}) in FT-IR spectra. The appearance of signal at δ 6.32 (β-1H), well apart from those of the signals for β-hydrogen atoms (6H) of the 2,5-disubstituted pyrrole (δ 5.83–5.99) in the ^{1}H NMR spectra and the appearance of four peaks for methyl C, four peaks for *meso*-C, seven peaks for β-pyrrolic CH and one peak for azo-substituted β-pyrrole C in the ^{13}C NMR spectra, confirmed the loss of symmetry in **4a**. Under negative ion ESI-MS, **4a** resulted in $[M - H]^-$ ion along with $[M + Cl]^-$ ion at low cone voltage. A detailed study of **1** and related macrocycles has been recently carried out by ESI-MS (*46*).

Anion binding with chromophoric calix[4]pyrroles (4a–4f)

The anion sensing ability of compounds **4a**–**4f** was studied on a qualitative level by visual examination of the anion-induced colour changes in the solution of sensors **4a**–**4f** (5.0×10^{-4} M in DMSO) before and after the addition of an anion. Compounds **4b**–**4f** showed dramatic colour changes in the presence of fluoride ion at room temperature, while **4a** did not give any noticeable colour change with different anions. For example, azo-sensors **4b**–**4d** (5.0×10^{-4} M in DMSO) appended with electron-donating substituents changed from light yellow to orange and dark brown, respectively, in the presence of F^- (5.0×10^{-3} M in DMSO) (Figure 1(a)). On the other



Scheme 1.

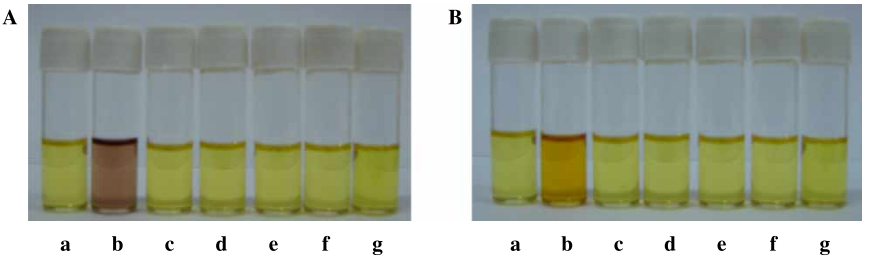


Figure 1. (**A**) Colour changes of **azo-4d** (5.0×10^{-4} M) in DMSO with the addition of tetrabutylammonium anions (5.0×10^{-3} M); (a) free receptor, (b) fluoride, (c) chloride, (d) bromide, (e) iodide, (f) hydrogen sulphate, (g) dihydrogen phosphate. (**B**) Colour changes of **azo-4e** (5.0×10^{-4} M) in DMSO with the addition of tetrabutylammonium anions (5.0×10^{-3} M); (a) free receptor, (b) fluoride, (c) chloride, (d) bromide, (e) iodide, (f) hydrogen sulphate, (g) dihydrogen phosphate.

hand, azo-sensors **4e** and **4f** (5.0×10^{-4} M in DMSO) appended with electron-withdrawing substituents changed the colour of the solution from yellow to brown and light brown, respectively, in the presence of F^- (5.0×10^{-3} M) (Figure 1(b)). Conversely, all the sensors except **4f** were found to be insensitive to the addition of a large excess of Cl^-, Br^-, I^-, HSO_4^- and $H_2PO_4^-$ (up to 20 equiv.). Furthermore, the addition of chloride and dihydrogen phosphate changed the colour of **4f** from yellow to light orange indicating significant binding of these anions with **azo-4f**. Thus, visual inspection of solutions of azo-OMCPs before and after the addition of anions indicate that fluoride ion interact more strongly due to higher electronegativity and smaller size compared with other anions (*47*, *48*).

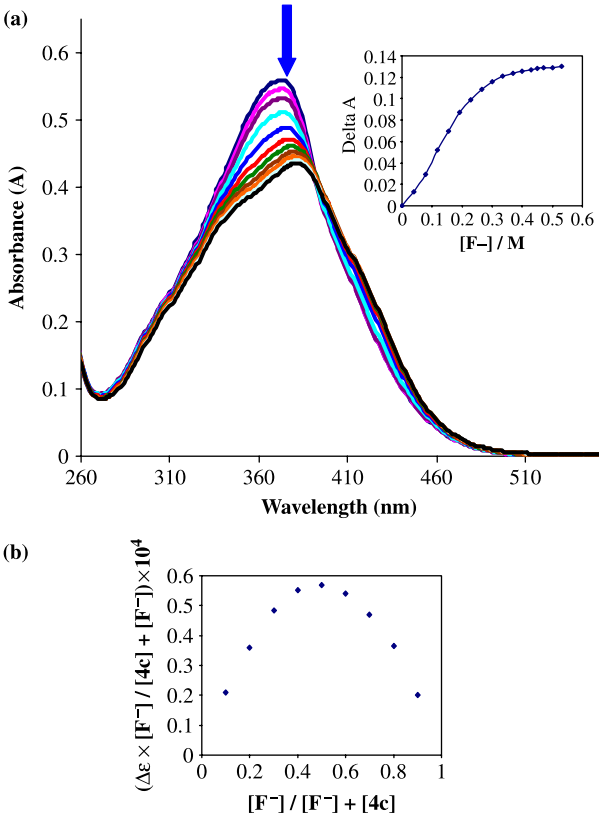


Figure 2. (a) The absorption spectra of **azo-4c** (5.0×10^{-4} M) in DMSO solution upon addition of 20 μl of stock solutions (5.0×10^{-4} M) of tetrabutylammonium fluoride. Inset: The changes in the 373 nm band as a function of fluoride anion. (b) Job plot for **azo-4c** with F^-.

UV–vis spectroscopy

The complexation studies of azo-OMCPs **4a**–**4f** were carried out with the help of UV–vis spectroscopy in DMSO at room temperature. Titrations were performed by adding aliquots of 20 μl of stock solutions (5.0×10^{-4} M) of anionic guests (F^-, Cl^-, Br^-, I^-, HSO_4^- and $H_2PO_4^-$) to the investigated derivatives **4a**–**4f** (5.0×10^{-4} M). For instance, the UV–vis spectra of **4c** showed a characteristic absorption maximum at 373 nm. With the addition of fluoride anion, peak at 373 nm gradually decreased with a bathochromic shift, meanwhile two clear isosbestic points were observed at 263 and 290 nm (Figure 2). The isosbestic points in the UV–vis spectra indicate that there is a balance in the solution and the complex has been formed between host and guest. The graph in the top right corner of the absorption spectra (Figure 2, inset) illustrates the absorbance changes of receptor solution upon addition of fluoride at 373 nm. Similar phenomenon was recognised with chloride; however, the addition of bromide, iodide and dihydrogen phosphate did not cause any significant spectral change even when a high excess of anion was employed, indicating that these anions form no (or very weak) complexes with **azo-4c**. The analogous binding affinity towards lighter halides, particularly fluoride, and to a lesser extent chloride, was observed with **azo-4b** and **azo-4d**. The qualitative changes are reflected in more quantitative terms in the UV–vis absorption spectra of **azo-4e** and **azo-4f**. With the addition of fluoride anion to the solution of **azo-4e** (5.0×10^{-4} M), the absorption maxima at 360 nm gradually decreased with considerable hypsochromic shift and two clear isosbestic points at 275 and 380 nm appeared along with new absorption maxima at 440 nm (Figure 3). Likewise, with **azo-4f**, the maxima

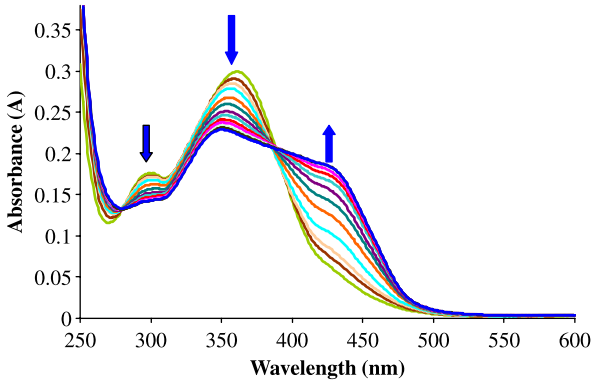


Figure 3. The absorption spectra of **azo-4e** (5.0×10^{-4} M) in DMSO solution upon addition of 20 μl of stock solutions (5.0×10^{-4} M) of tetrabutylammonium fluoride.

at 412 nm decreased and two new maxima located at 364 and 475 nm were observed when fluoride was added to the receptor solution. The new absorption peaks at 440 and 475 nm can be ascribed to partial charge-transfer interactions between the electron-rich donor nitrogen atom of pyrrole moieties and the electron-deficient *p*-chloro/nitro phenyl units.

An important additional observation made during these experiments is that the spectra as well as the colour of the solution of receptor-F^- conjugates revert back to the original spectra corresponding to those receptors in the absence of anion upon addition of small aliquots of water/methanol. This phenomenon illustrates that the addition of a protic solvent destroyed the complexation between **4** and F^-, demonstrating that interaction between **4** and F^- was, in essence, a hydrogen-bonding interaction.

Continuous variation methods were used to determine the stoichiometric ratios of the complexes formed between the azo-OMCPs and the anion guests. In all cases, 1:1 stoichiometry was recognised. The quantitative titration experiments allowed us to determine apparent binding constants for **4a**–**4f** with different anions. Binding constants were calculated as described in the literature (*47*). The respective K_{ass} values are summarised in Table 1. As shown in Table 1, **azo-4e** and **azo-4f** display a higher affinity for fluoride anion compared with the other azo-sensors. The strong binding is ascribed to the electron-withdrawing nature of dye moieties. These moieties increase the acidity of the pyrrole NH proton, which in turn enhances the availability of NHs for hydrogen bonding and affinity of sensors towards anions.

^{1}H NMR spectroscopy

It is well known that the competing processes that are not always immediately recognised can complicate apparently simple anion complexation processes, especially with more basic anions like fluoride and acetate (*49*, *50*). To probe the actual anion binding, ^{1}H NMR titrations were performed in $CDCl_3$ with fluoride anion. Titration experiments revealed that anion binding is a prevalent process.

Table 1. Association constants (K_{ass})[a] of compounds azo-OMCP **4a**–**4f** with a variety of putative anionic guests at 25°C in DMSO solution.

	Association constant K_{ass} (M^{-1})					
Anion[b]	**Azo-4a**	**Azo-4b**	**Azo-4c**	**Azo-4d**	**Azo-4e**	**Azo-4f**
F^-	298	4870	$>10^4$	$>10^4$	$>10^5$	$>10^5$
Cl^-	n.d.	23	583	615	122	750
Br^-	n.d.	<50	>35	<50	<50	n.d.
I^-	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
HSO_4^-	n.d.	73	67	n.d.	<50	89
$H_2PO_4^-$	n.d.	n.d.	2523	2925	n.d.	3100

[a] Determined from absorption spectroscopic titrations.
[b] Anions were used in the form of their (TBA) salts.

Significant downfield shifts of the pyrrole NH protons (3.0–5.5 ppm) were observed upon addition of F^- in $CDCl_3$ solution of **4a**–**4f**. The observed downfield shifts of the pyrrole NH resonances are an indication of hydrogen bonding to fluoride anion, as well as simplification of the pyrrole CH signals, a characteristic for transition from 1,3 alternate to a symmetrical cone-like conformation. As an example, the ^{1}H NMR spectral changes upon addition of F^- to the $CDCl_3$ solution of **azo-4c** are shown in Figure 4. The pyrrole NH resonances of **4c** at δ 7.31 (2H), δ 7.00 (1H) and δ 6.94 ppm (1H) were initially disappeared upon addition of 0.2 equiv. of F^- and a new broad signal appeared at δ 7.92. On the successive addition of aliquots of F^-, the signal gradually shifted from δ 7.92 to 11.6 ppm and finally split into four distinct singlets that appear at δ 12.37, 12.78, 12.90 and 13.19 ppm, respectively, suggesting NH—F^- complexation.

A careful examination of the spectral changes in the ^{1}H NMR spectra of **4a**–**4f** containing different concentrations of F^- reveals that the β-proton (C_3—H) on the pyrrole ring represents a dramatic upfield shift. In the case of **4c**, the β-proton (C_3—H) shifted upfield by δ 0.34 ppm with the addition of 1.25 equiv. of F^-. It is worthy to note that according to previous studies, F^- seems to interact with a hydrogen bond donor —OH as a binding site (*51*, *52*), but with **azo-4c**, the phenolic proton remained almost unchanged throughout the titration, indicating the minimal interaction between —OH and F^-. Further, insight into anion complexation was achieved by titrating **azo-4f** with fluoride anion in DMSO-d_6 and $CDCl_3$, respectively. It was found that the addition of increasing amounts of fluoride anion to **4f** caused significant downfield shifts in the NH protons in moving from DMSO-d_6 to $CDCl_3$. This indicates that the former

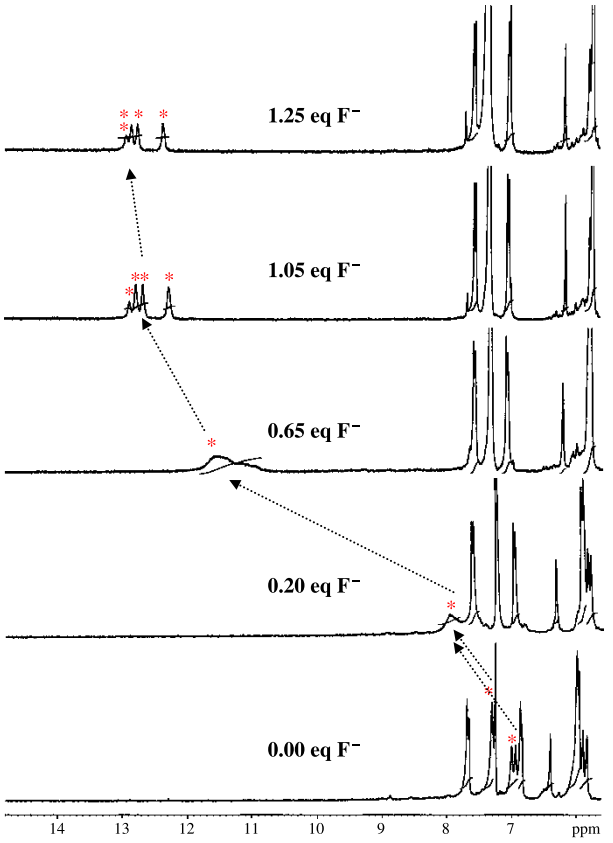


Figure 4. ^{1}H NMR spectra of **azo-4c** (5.0×10^{-4}) in $CDCl_3$ solution at 25°C upon addition of aliquots of tetrabutylammonium fluoride.

solvent is liable to interact with **4f** through hydrogen bond formation between the NH protons and the basic oxygens of the solvent. Therefore, the ability of **4f** to interact with F^- is likely to be significantly reduced in DMSO-d_6 relative to $CDCl_3$. Consistent and reproducible results were obtained with other azo-sensors.

Conclusion

The anion-binding properties of synthesised sensors **4a–4f** were studied by the UV–vis and ^{1}H NMR spectroscopic techniques. Binding constants calculated by absorption spectroscopic titrations indicate that OMCP-based sensors **azo-4a–4f** favour spherical anions, principally fluoride and chloride. On the contrary, the anions with low surface charge density such as bromide and iodide form weak or no adducts. The specific order of binding affinities is as follows: **azo-4f** ~ **azo-4e** > **azo-4c** ~ **azo-4d** > **azo-4b**. Accordingly, the incorporation of electron-withdrawing (chloro and nitro) groups in azo-calix[4]pyrrole skeleton gave higher binding constants than electron-donating (hydroxyl and methoxy) groups, nevertheless equally are able to sense the F^- successfully with naked eye. Colorimetric sensing of fluoride displayed by azo-OMCPs is important from the biological point of view and can be utilised for the nerve gas sarin (GB) (isopropyl methylphosphonofluoridate) that loses a fluoride anion during hydrolysis.

Experimental

All the quaternary ammonium salts such as *n*-Bu_4NF, *n*-Bu_4NCl, *n*-Bu_4NBr, *n*-Bu_4NI, Bu_4NHSO_4 and $Bu_4NH_2PO_4$ were purchased from Aldrich and dried under high vacuum at 40°C for 24 h before use. HPLC-grade solvents were used in the assay. Column chromatography was carried out on Merck silica gel (60–120 mesh). ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance 300 spectrophotometer. ^{1}H NMR chemical shift values (300 MHz) are reported as δ using the residual solvent signal as an internal standard (DMSO, δ 2.49; $CDCl_3$, δ 7.29). The infrared spectra (IR) were recorded on Perkin–Elmer FT-1710 spectrophotometer and only characteristic absorptions are reported. Electrospray ionisation (ESI) spectra were recorded on KC 455 time-of-flight (TOF) mass spectrometer (Micromass, Manchester, UK).

*Synthetic protocol for the preparation of 2-arylazo-***meso-*octamethylcalix[4]pyrroles***

A solution of phenyldiazonium chloride, prepared from aniline derivatives (2.5 mmol), sodium nitrite (2.5 mmol) and conc. HCl (1.3 ml) in water (2 ml), was added slowly to a cold (−10°C) solution of OMCP **1** (1.0 g, 2.34 mmol) and sodium hydrogen carbonate in THF (50 ml) to give a dark yellow suspension. After stirring for 20 min, the solution was diluted with water and extracted with ethyl acetate. Organic extracts were washed twice with water and dried over anhydrous magnesium sulphate. The solvent was evaporated under reduced pressure. Chromatographic workup (ethyl acetate–petroleum ether, 0.5:10, v/v) of crude product afforded 2-arylazo-*meso*-Octamethylcalix[4]pyrroles.

Meso-*octamethylcalix[4]pyrrole* (***1***)

White solid; yield: 84%; m.p.: 295°C; IR (KBr pellet, cm^{-1}): 3435 (br, pyrrole NH), 3023, 2842, 1541, 1187, 752; ^{1}H NMR (300 MHz, 25°C, $CDCl_3$): δ 1.50 (24H, s, —CH_3), 5.89 (8H, d, β-pyrrolic), 7.01 (4H, s, pyrrole NH); ^{13}C NMR (75 MHz, $CDCl_3$, 25°C, TMS): δ 29.0 CH_3, 35.1 *meso*-C, 102.7 pyrrole β-CH, 138.3 pyrrole α-C; HR-MS (ESI-MS) for $C_{28}H_{36}N_4$ $[M - H]^-$: calcd, 427.2862; found, 427.2860.

N-Confused octamethylcalix[4]pyrrole (***2***)

White solid; yield: 14%; m.p.: 185°C; IR (KBr pellet, cm^{-1}): 3430, 2910, 2845, 1521, 1616, 1179, 749; ^{1}H

NMR (300 MHz, $CDCl_3$, 25°C): δ 1.48–1.54 (m, 24H, —CH_3), 5.07 (br, 1H, β-pyrrolic), 5.87 (m, 2H, β-pyrrolic), 5.89 (br, 2H, β-pyrrolic), 5.90 (br, 2H, β-pyrrolic), 6.51 (d, 1H, α-pyrrolic), 6.97 (br, 1H, pyrrole NH), 7.13 (br, 1H, pyrrole NH), 7.48 (br, 1H, pyrrole NH), 7.76 (br, 1H, pyrrole NH); ^{13}C NMR (75 MHz, $CDCl_3$, 25°C, TMS): δ 29.0 CH_3, 29.4 CH_3, 29.6 CH_3, 30.34 CH_3, 34.6 C, 35.3 C, 35.7 C, 35.9 C, 101.6 CH, 101.8 CH, 102.1 CH, 102.8 CH, 103.3 CH, 103.9 CH, 104.2 CH, 111.6 CH, 133.2 C, 137.5 C, 137.8 C, 138.2 C, 138.7 C, 138.8 C, 139.4 C, 141.1 C; HR-MS (ESI-MS) for $C_{28}H_{36}N_4$ $[M - H]^-$: calcd, 427.2862; found, 427.2859.

*2-Phenyl-azo-5,10,15,20-octamethylcalix[4]pyrrole (**4a**)*

Yellow solid; yield: 17%; m.p.: 198°C; IR (KBr pellet, cm^{-1}): 3441 (br, pyrrole NH), 3046 (—CH aryl), 2930, 1648, 1598 (N═N), 780, 530; ^{1}H NMR (300 MHz, 25°C, $CDCl_3$): δ 1.50–1.53 (m, 18H, CH_3), 1.85 (s, 6H, CH_3) 5.83–5.99 (m, 6H, β-pyrrolic CH), 6.32 (s, 1H, β-pyrrolic CH), 6.92 (s, 1H, pyrrole NH), 7.05 (s, 1H, pyrrole NH), 7.37 (s, 2H, pyrrole NH), 7.43–7.48 (m, 3H, aryl CH), 7.75–7.78 (d, $J = 8.1$ Hz, 2H, aryl CH); ^{13}C NMR (75 MHz, 25°C, $CDCl_3$): δ 26.35 CH_3, 27.34 CH_3, 27.52 CH_3, 28.20 CH_3, 33.56 C, 35.20 C, 35.31 C, 36.40 C, 92.42 CH, 101.16 CH, 101.97 CH, 102.66 CH, 103.14 CH, 103.22 CH, 103.80 CH, 112.82 CH, 113.62 CH, 121.43 CH, 135.92 C, 137.00 C, 137.44 C, 137.91 C, 138.10 C, 138.34 C, 139.00 C, 139.10 C, 141.20 C, 144.36 C, 144.42 C; ESI-MS for $C_{34}H_{40}N_6$: 531 ($[M - H]^-$, 100%), 532 ($[M]^-$, 18%); 567 ($[M + Cl]^-$, 10%); $R_f = 0.40$ (ethyl acetate–petroleum ether, 1:10 v/v).

*2-(4′-Methylphenyl)-azo-5,10,15,20-octamethylcalix[4]-pyrrole (**4b**)*

Brown solid; yield: 23%; m.p.: 202°C; IR (KBr pellet, cm^{-1}): 3435 (br, pyrrole NH), 3030 (—CH aryl), 2924, 1682, 1613 (N═N), 767, 551; UV–vis (λ_{max}, $CHCl_3$): 367 nm; ^{1}H NMR (300 MHz, 25°C, $CDCl_3$): δ 1.25 (s, 6H, CH_3), 1.50 (m, 12H, CH_3), 1.87 (s, 6H, CH_3), 2.40 (s, 3H, aryl-CH_3) 5.83 (s, 1H, β-pyrrolic CH), 5.90 (s, 1H, β-pyrrolic CH), 5.94–5.96 (m, 4H, β-pyrrolic CH), 6.38 (s, 1H, β-pyrrolic CH), 6.84 (d, $J = 6.6$ Hz, 2H, aryl CH), 6.94 (s, 1H, pyrrole NH), 7.00 (s, 1H, pyrrole NH), 7.31 (s, 2H, pyrrole NH), 7.66–7.69 (d, $J = 7.8$ Hz, 2H, aryl CH); ^{13}C NMR (75 MHz, 25°C, $CDCl_3$): δ 28.41 CH_3, 28.65 CH_3, 28.71 CH_3, 29.40 CH_3, 32.56 CH_3, 34.55 C, 35.14 C, 35.34 C, 36.47 C, 92.53 CH, 100.36 CH, 102.57 CH, 102.96 CH, 103.24 CH, 103.87 CH, 104.00 CH, 113.56 CH, 121.75 CH, 136.42 C, 137.20 C, 137.64 C, 138.10 C, 138.23 C, 138.54 C, 139.13 C, 139.33 C, 141.24 C, 146.56 C, 155.42 C; ESI-MS for $C_{35}H_{42}N_6$: 545 ($M - H]^-$,100%), 546 ($[M]^-$, 29%); $R_f = 0.50$ (ethyl acetate–petroleum ether, 1:10 v/v).

*2-(4′-Hydroxyphenyl)-azo-5,10,15,20-octamethylcalix[4]-pyrrole (**4c**)*

Lemon yellow solid; yield 65%; m.p.: 210°C; IR (KBr pellet, cm^{-1}): 3435 (br, pyrrole NH), 3262 (—OH aryl), 3046 (—CH aryl), 2997, 1648, 1587 (N═N), 1371, 1303, 989, 793, 547; UV–vis (λ_{max}, $CHCl_3$): 373 nm; ^{1}H NMR (300 MHz, 25°C, $CDCl_3$): δ 1.51–1.53 (m, 18H, CH_3), 1.82 (s, 6H, CH_3), 5.20 (s, 1H, phenolic-OH), 5.84 (s, 1H, β-pyrrolic CH), 5.90 (s, 1H, β-pyrrolic CH), 5.96–5.99 (m, 4H, β-pyrrolic CH), 6.40 (s, 1H, β-pyrrolic CH), 6.84 (d, $J = 8.1$ Hz, 2H, aryl CH), 6.94 (s, 1H, pyrrole NH), 7.00 (s, 1H, pyrrole NH), 7.31 (s, 2H, pyrrole NH), 7.66 (d, $J = 8.1$ Hz, 2H, aryl CH); ^{13}C NMR (75 MHz, 25°C, $CDCl_3$): δ 28.61 CH_3, 28.75 CH_3, 29.27 CH_3, 29.61 CH_3, 35.15 C, 35.24 C, 35.40 C, 37.47 C, 93.73 CH, 101.61 CH, 102.87 CH, 103.27 CH, 103.82 CH, 104.00 CH, 104.14 CH, 115.68 CH, 123.69 CH, 137.00 C, 137.42 C, 137.75 C, 138.21 C, 138.31 C, 138.85 C, 139.39 C, 139.43 C, 141.57 C, 147.98 C, 156.60 C; ESI-MS for $C_{34}H_{40}N_6O$: 547 ($[M - H]^-$, 100%), 548 ($[M]^-$, 64%); 583 ($[M + Cl]^-$, 38%); $R_f = 0.82$ (ethyl acetate–petroleum ether, 1:10 v/v).

*2-(4′-Methoxyphenyl)-azo-5,10,15,20-octamethylcalix[4]-pyrrole (**4d**)*

Light orange solid; yield: 35%; m.p.: 206–207°C; IR (KBr pellet, cm^{-1}): 3443 (br, pyrrole NH), 3099 (—CH aryl), 2968, 2874, 1682, 1607 (N═N), 1303, 1157, 1030 (—OCH_3), 767, 551; UV–vis (λ_{max}, $CHCl_3$): 372 nm; ^{1}H NMR (300 MHz, 25°C, $CDCl_3$): δ 1.52–1.53 (m, 18H, CH_3), 1.84 (s, 6H, CH_3), 3.86 (s, 3H, —OCH_3), 5.85–5.98 (m, 6H, β-pyrrolic CH), 6.42 (s, 1H, β-pyrrolic CH), 6.87 (d, $J = 8.1$ Hz, 2H, aryl CH), 6.96 (s, 1H, pyrrole NH), 7.00 (s, 1H, pyrrole NH), 7.33 (m, 2H, pyrrole NH), 7.66 (d, $J = 8.1$ Hz, 2H, aryl CH); ^{13}C NMR (75 MHz, 25°C, $CDCl_3$): δ 27.61 CH_3, 28.10 CH_3, 28.97 CH_3, 29.42 CH_3, 35.20 C, 35.38 C, 35.48 C, 37.53 C, 62.56 OCH_3, 92.30 CH, 100.60 CH, 102.26 CH, 103.10 CH, 103.64 CH, 103.89 CH, 104.24 CH, 115.28 CH, 122.32 CH, 136.80 C, 136.22 C, 136.46 C, 137.92 C, 138.10 C, 138.45 C, 139.00 C, 139.47 C, 140.90 C, 147.80 C, 155.30 C; ESI-MS for $C_{35}H_{42}N_6O$: 561 ($[M - H]^-$,100%), 562 ($[M]^-$, 80%); $R_f = 0.80$ (ethyl acetate–petroleum ether, 1:10 v/v).

*2-(4′-Chloro phenyl)-azo-5,10,15,20-octamethylcalix[4]-pyrrole (**4e**)*

Yellow solid; yield: 47%; m.p.: 160°C; IR (KBr pellet, cm^{-1}): 3436 (br, pyrrole NH), 3025 (CH aryl), 2925, 2853, 1627 (N═N), 700, 640; UV–vis (λ_{max}, $CHCl_3$): 373 nm; ^{1}H NMR (300 MHz, 25°C, $CDCl_3$): δ 1.28

(s, 6H, CH_3), 1.50 (s, 12H, CH_3), 1.83 (s, 6H, CH_3), 5.88–5.89 (m, 4H, β-pyrrolic CH), 5.96–5.99 (m, 2H, β-pyrrolic CH), 6.42 (s, 1H, β-pyrrolic CH), 6.87 (d, $J = 8.1$ Hz, 2H, aryl CH), 6.94 (s, 2H, pyrrole NH), 7.34 (s, 2H, pyrrole NH), 7.75–7.78 (d, $J = 8.1$ Hz, 2H, aryl CH); ^{13}C NMR (75 MHz, 25°C, $CDCl_3$): δ 28.58 CH_3, 29.12 CH_3, 29.89 CH_3, 30.74 CH_3, 34.83 C, 34.85 C, 35.29 C, 38.04 C, 93.16 CH, 102.14 CH, 102.49 CH, 102.99 CH, 103.25 CH, 103.85 CH, 104.34 CH, 122.53 CH, 125.53 CH, 136.91 C, 137.23 C, 138.71 C, 138.76 C, 139.26 C, 139.73 C, 140.62 C, 141.50 C, 146.31 C, 147.26 C, 157.19 C; ESI-MS for $C_{34}H_{39}N_6Cl$: 565 ($[M - H]^-$, 100%), 566 ($[M]^-$, 50%); $R_f = 0.32$ (ethyl acetate–petroleum ether, 1:10 v/v).

*2-(4′-Nitro phenyl)-azo-5,10,15,20-octamethylcalix[4]-pyrrole (**4e**)*

Yield: 15%; m.p.: 259°C; ESI-MS for $C_{34}H_{39}N_7O_2$: 576 ($[M - H]^-$, 100%), 577 ($[M]^-$, 80%); $R_f = 0.60$ (ethyl acetate–petroleum ether, 1:10 v/v).

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