

Fig. 1 X-Ray crystal structure of compound **1c**. Thermal ellipsoids are drawn at the 35% probability level. Most hydrogen atoms have been removed for clarity.

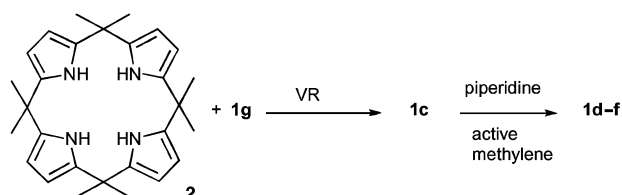
separated without difficulty by column chromatography, **1g** being the more polar isomer. However, because the “NMR yield” is higher than the isolated yield, we conclude that some of the slightly unstable **1g** is lost during chromatography.

We have found it convenient to take the crude calixpyrrole mixture and subject it directly to electrophilic substitution, in this case formylation with the Vilsmeier reagent (VR). We can take advantage of the fact that the α -position of **1g** is much more reactive than the β -positions of **2**. Moreover, the aldehyde of **1c** increases in polarity compared to **1g**, so chromatography becomes more straightforward. This gives a 62% yield of **1c**, based on the amount of **1g** in the starting mixture, according to ^1H NMR spectroscopy. Interestingly, when isolated **1g** was used instead of the **2/1g** mixture, only a 42% yield of **1c** was obtained. One possible explanation for this is that the excess of **2** protects the *N*-confused isomer from ring cleavage caused by the hydrochloric acid generated under the reaction conditions.

With multi-gram amounts of **1c** available, we turned our attention to its Knoevenagel condensation reaction with active methylenes. Reaction of **1c** under standard conditions with, respectively, 1-oxoinden-3-ylidenemalonitrile, phenalene-1,3-dione and Meldrum's acid afforded the coloured *N*-confused calix[4]pyrrole derivatives **1d–f** in 53–81% yield (Scheme 1).

X-Ray crystallography

The structure of the *N*-confused calix[4]pyrrole derivatives **1c**, **1d** and **1f** have been unequivocally confirmed by single-crystal X-ray diffraction studies. Crystals of compound **1c** were



Scheme 1

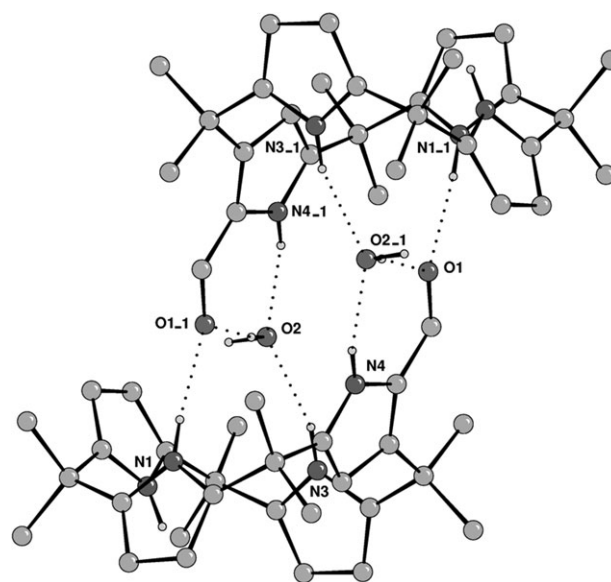


Fig. 2 Hydrogen bonding in compound **1c**. Disorder (10%) omitted for clarity ($i = 1 - x$, $1 - y$, $1 - z$).

grown by slow evaporation of a MeCN/ CH_2Cl_2 solution of the receptor (Fig. 1).§

As the inverted pyrrole ring is linked through its α' - and β -positions (C22 and C24, respectively) instead of its α - and α' -positions (C23 and C24, respectively), as in ‘regular’ calix[4]pyrrole **2**, we can regard this structure as a confused-1,3-alternate arrangement.^{2,11} The typical 1,3-alternate conformation of calix[4]pyrroles is often observed in crystal structures of free calix[4]pyrrole **2** and solvates of the macrocycle. Notably, the aldehyde moiety is coplanar with respect to the inverted pyrrole unit. The molecule dimerizes *via* pyrrole NH–aldehyde-oxygen hydrogen bonds (Fig. 2).

Crystals of compound **1d** were grown by slow evaporation of a MeCN/ CH_2Cl_2 solution of the receptor (Fig. 3).¶ Compound **1d** adopts a very similar conformation to the *N*-confused calix[4]pyrrole **1c**, showing the same arrangement of the macrocyclic core, as well as the coplanarity of the oxoindenylidenemalonitrile moiety with the methine bridge and the inverted pyrrole unit. Moreover, in this case, an acetonitrile is coordinated *via* a hydrogen bond to one of the non-inverted NH groups. An intramolecular interaction between the oxygen

§ Crystal data for **1c**: $\text{C}_{29}\text{H}_{37.80}\text{N}_4\text{O}_{1.90}$, $M_r = 472.83$, $T = 120(2)$ K, triclinic, space group $P-1$, $a = 10.1714(3)$, $b = 10.1756(3)$, $c = 13.1069(4)$ Å, $\alpha = 107.535(2)^\circ$, $\beta = 92.714(2)^\circ$, $\gamma = 91.380(2)^\circ$, $V = 1291.03(7)$ Å³, $\rho_{\text{calc}} = 1.218$ g cm^{−3}, $\mu = 0.077$ mm^{−1}, $Z = 2$, reflections collected: 29203, independent reflections: 5888 ($R_{\text{int}} = 0.0531$), final R indices [$I > 2\sigma(I)$]: $R_1 = 0.0741$, $wR_2 = 0.1899$, R indices (all data): $R_1 = 0.1158$, $wR_2 = 0.2117$. CCDC 624049. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b616467f

¶ Crystal data for **1d**: $\text{C}_{41}\text{H}_{40}\text{N}_6\text{O} \cdot 0.5(\text{C}_2\text{H}_3\text{N})$, $M_r = 653.32$, $T = 120(2)$ K, monoclinic, space group $P2_1/c$, $a = 19.7663(15)$, $b = 11.8837(8)$, $c = 15.7559(14)$ Å, $\beta = 106.807(4)^\circ$, $V = 3542.9(5)$ Å³, $\rho_{\text{calc}} = 1.225$ g cm^{−3}, $\mu = 0.076$ mm^{−1}, $Z = 4$, reflections collected: 35967, independent reflections: 7024 ($R_{\text{int}} = 0.1582$), final R indices [$I > 2\sigma(I)$]: $R_1 = 0.0907$, $wR_2 = 0.2159$, R indices (all data): $R_1 = 0.2209$, $wR_2 = 0.2756$. CCDC 624050. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b616467f

Table 1 Stability constants K_a (M^{-1}) of compounds **1c–f** with a variety of putative anionic guests (added as tetrabutylammonium salts) at 298 K in DMSO- d_6 -0.5% water,^a as determined by 1H NMR techniques. In all cases 1 : 1 receptor : anion stoichiometry was observed

Anion	Compounds				
	1c	1d	1e	1f	1g
Cl^-	30	118	94	135	17
Br^-	<10	<10	<10	<10	<10
$CH_3CO_2^-$	499	1241	879	1373	75
$C_6H_5CO_2^-$	129	629	313	542	45
$H_2PO_4^-$	38	197	176	194	20
HSO_4^-	<10	<10	<10	<10	<10

^a Errors estimated to be no more than $\pm 10\%$.

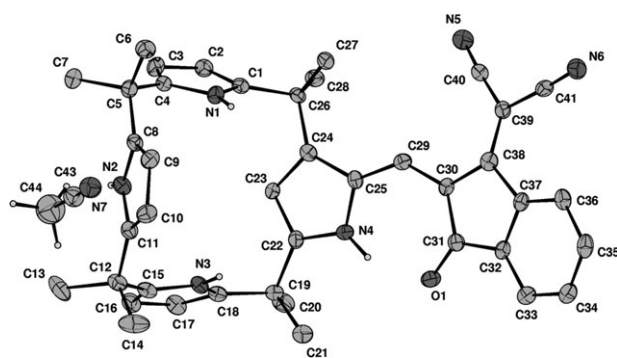


Fig. 3 X-Ray crystal structure of compound **1d**. Thermal ellipsoids are drawn at the 30% probability level. Most hydrogen atoms have been removed for clarity.

of the oxoindenylidene group and the NH of the inverted pyrrole (Fig. 3) is also observed. Representative bond distances are: $N2 \cdots N7$ 3.291(8) Å and $N4 \cdots O1$ 2.639(5) Å. Representative bond angles are: $N-H \cdots N$ 173(3)° and $N-H \cdots O$ 149(8)°. In the solid state, compound **1d** forms a hydrogen-bonded dimer *via* the interaction of a non-inverted NH group of one monomer with one nitrogen of the malonitrile moiety belonging to a second monomer (see Fig. 4). The bond distance observed is $N3 \cdots N6^i$ 3.068(6) Å, with a $N-H \cdots N$ bond angle of 162(1)° (symmetry codes: $i = -x + 1, y, -z + \frac{1}{2}$).

Finally, crystals of compound **1f** were obtained by slow evaporation of a DMSO solution of the complex. The structure is shown in Fig. 5. Once again, the structure of compound **1f** in the solid state shows coordination of one molecule of solvent, in this case DMSO, coordinated through an intermolecular interaction with one of the non-inverted NH groups. Moreover, an intramolecular interaction between the oxygen of the 1,3-dioxane-4,6-dione moiety and the NH of the inverted pyrrole is observed. Representative bond distances for both interactions are: $N1 \cdots O9$ 3.020(7) Å and $N2 \cdots O2$

2.658(7) Å, with $N-H \cdots O$ bond angles being 168(2) and 146(0)°, respectively. Otherwise, the structure presents the same characteristics as described for complexes **1c** and **1d**.

Complexation studies

Initial complexation studies on *N*-confused calix[4]pyrroles **1c–f** were conducted using 1H NMR titration techniques. Aliquots of tetrabutylammonium salts of putative anionic guests (0.1 M) were added to a solution of compounds **1c–f** (0.01 M) in DMSO- d_6 -0.5% water. The resulting stability constants are summarized in Table 1.

The addition of bromide and hydrogen sulfate did not cause any significant spectral change, even when a large excess of anion was employed. Thus, these anions form no (or very weak) complexes with compounds **1c–f** ($K_a < 10 M^{-1}$, see Table 1). On the other hand, analysis of the remaining titration data using the EQNMR¹² computer program revealed that these compounds form 1 : 1 receptor : anion complexes with chloride, acetate, benzoate and dihydrogen phosphate anions, showing a moderate-to-low affinity of receptors **1c–f** for these anions in this competitive solvent medium ($CH_3CO_2^- > C_6H_5CO_2^- > H_2PO_4^- > Cl^-$, Table 1).¹³ In order to evaluate the effect that the different substituents at the α -position of the *N*-confused calix[4]pyrroles (**1c–f**) have on anion affinity, complexation studies with compound **1g** were conducted using the same solvent conditions (see Table 1). The stability constants of derivative **1g** with anions are much lower than those obtained for compounds **1c–f**, indicating that the substituents are playing an important role. This behaviour may be attributed to the electron-withdrawing properties of these groups.

Significant downfield shifts of the pyrrole NH protons were observed upon addition of anions, consistent with the formation of *N*-confused calix[4]pyrrole–anion hydrogen bonds. As an example, the 1H NMR spectral changes upon addition of tetrabutylammonium acetate to the DMSO- d_6 -0.5% water solution of compound **1f** are shown in Fig. 6.

Increasing the concentration of acetate anion in the host–guest mixture solution induced a clear downfield shift in the NH peaks of the non-inverted pyrroles (NH), whereas a slight upfield shift of the pyrrole β -H signals (β -CH) was observed. Otherwise, the inverted pyrrole showed a concerted upfield shift of the pyrrole NH signal (NH_i) as well as a pronounced downfield shift of the β -pyrrole proton (β -CH_i).

|| Crystal data for **1f**. $C_{35}H_{42}N_4O_4 \cdot (C_2H_6OS)$, $M_r = 1321.71$, $T = 120(2)$ K, monoclinic, space group $P2_1/c$, $a = 10.1460(2)$, $b = 26.3142(9)$, $c = 26.8959(9)$ Å, $\beta = 98.040(2)^\circ$, $V = 7110.2(4)$ Å³, $\rho_{calc} = 1.235$ g cm⁻³, $\mu = 0.138$ mm⁻¹, $Z = 8$, reflections collected: 76382, independent reflections: 13971 ($R_{int} = 0.1523$), final R indices [$I > 2\sigma(I)$]: $R_1 = 0.1076$, $wR_2 = 0.2649$, R indices (all data): $R_1 = 0.1950$, $wR_2 = 0.3182$. CCDC 624051. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b616467f

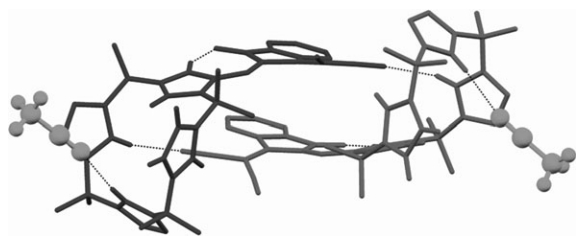


Fig. 4 Hydrogen-bonded dimer in the solid state of compound **1d**.

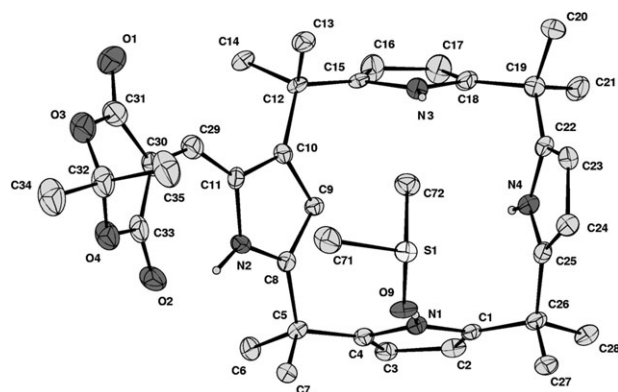


Fig. 5 X-Ray crystal structure of compound **1f**. Thermal ellipsoids are drawn at the 35% probability level. The non-acidic hydrogen atoms have been removed for clarity. The asymmetric unit contains two receptor and two DMSO molecules, only one of each is shown; the disorder in the receptor is omitted.

This fact is evidence for the formation of a $\beta\text{-CH}_i \cdots \text{anion}$ hydrogen bond in solution, suggesting that the anion coordinates to these *N*-confused calix[4]pyrrole receptors (**1c–f**) by the three NH groups of the non-inverted pyrroles as well as the $\beta\text{-CH}_i$ moiety of the inverted pyrrole. The ^1H NMR titrations of **1c–f** with all the anions show the same type of behaviour, suggesting the same binding mode in all the cases.

Therefore, the biggest variations found in the ^1H NMR spectra during these titrations belong to the non-inverted NH groups and to the $\beta\text{-CH}$ inverted pyrrole resonances. Unfortunately, in some cases, the NH signals of the non-inverted pyrroles (NH) cannot be followed owing to a significant broadening of the resonances during the titrations (*i.e.*, when using benzoate and dihydrogen phosphate tetrabutylammonium salts). On other occasions, the β -pyrrole proton of the inverted pyrrole ($\beta\text{-CH}_i$) was partially obscured during titrations (*i.e.*, in compounds **1d** and **1e**). However, in all cases, the shift changes in the inverted pyrrole NH signals (NH_i) of the anion added can be fitted to a 1:1 binding equilibrium profile as a function of the concentration. As an example, Fig. 7 shows the variation of the inverted pyrrole NH signal for compound **1f** in the presence of increasing amounts of tetrabutylammonium acetate.**

** Where possible, the NH resonances of the non-inverted pyrroles and the β -pyrrole proton of the inverted pyrrole have been also fitted, which was found to give a consistent K_a value to that observed from fitting the shift of the inverted pyrrole NH signal (see Table 1).

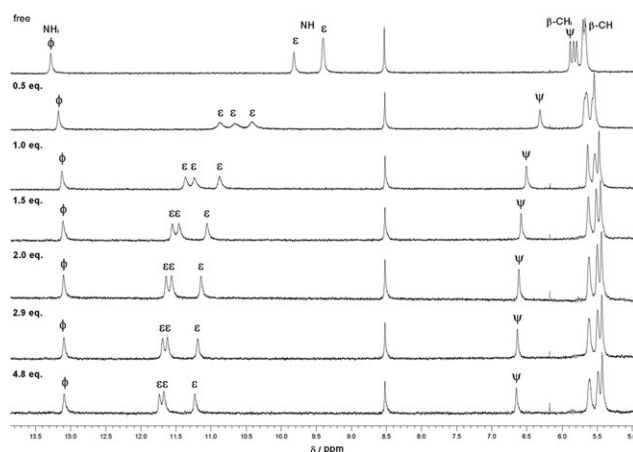


Fig. 6 ^1H NMR titrations (selected region) of a 0.01 M solution of **1f** with tetrabutylammonium acetate in $\text{DMSO-}d_6$ -0.5% water as solvent. The pyrrole ^1H resonances are labelled as follows: NH_i (ϕ), NH (ϵ) and $\beta\text{-CH}_i$ (ψ), where *i* = inverted or confused pyrrole ring.

It is worthy of note that these *N*-confused calix[4]pyrroles show a moderate selectivity towards carboxylate anions, especially acetate, over chloride and phosphate (see Table 1), which is consistent with the basicity of these anionic guests. This behaviour has been also recently described by Anzenbacher *et al.* for the azo- and tricyanoethenyl derivatives **1a,b**.⁸

Titration studies of these *N*-confused calix[4]pyrroles **1c–f** with tetrabutylammonium fluoride have been also performed. Unfortunately, the ^1H NMR spectra obtained show a significant broadening of all the NH and CH signals upon addition of the salt, making the determination of stability constants with this anion not possible by this method.

The chemistry of *N*-confused calix[4]pyrroles is still largely unexplored. These macrocycles are more amenable to functionalisation and also provide a different order of anion affinity to the calix[4]pyrroles. We are continuing to study the differences between the confused calixpyrroles and their 'regular' cousins.

Experimental

Melting points were determined with a Boetius Block apparatus and are uncorrected. ^1H and ^{13}C NMR spectra were

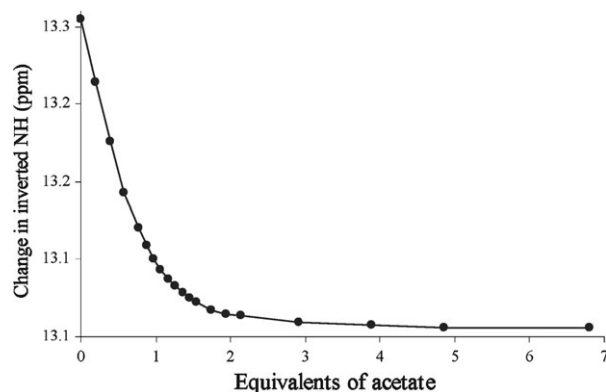


Fig. 7 Shifts of the inverted pyrrole NH signal in compound **1f** upon addition of tetrabutylammonium acetate in $\text{DMSO-}d_6$ -0.5% water.

recorded on Varian Mercury 300 MHz, Bruker Avance 300 MHz and Bruker AMX3 400 spectrometers using tetramethylsilane as an internal standard for compound characterisation. ES-MS were measured on a Micromass Mattro II instrument. ^1H NMR spectra for the titration experiments were recorded on a Bruker AV-300 NMR spectrometer. Chemical shifts are reported in ppm and referenced to the solvent for the binding studies. Deuterated solvents were purchased from Apollo Ltd.

Octamethyl *N*-confused calix[4]pyrrole aldehyde **1c**

To an 80 : 20 mixture of calix[4]pyrrole and *N*-confused calix[4]pyrrole (0.049 mol, 21 g) in dichloromethane (500 mL) was added triethylamine (0.078 mol, 11 mL). The mixture was cooled to a temperature of -78°C . Subsequently, (chloromethylene)dimethylammonium chloride (0.039 mol, 5 g) was added. The mixture was stirred for 5 h, the ice bath removed and stirring continued for another 30 min. The reaction was quenched by pouring it onto a mixture of ice (1 L) and sodium hydrogen carbonate (500 mL) while stirring. After reaching room temperature, the mixture was extracted with dichloromethane (3×100 mL), the organic layers dried over magnesium sulfate and evaporated to dryness. The crude brown-black solid was purified by column chromatography (silica) using dichloromethane–heptane (7 : 3), dichloromethane and dichloromethane–ethyl acetate (9 : 1) as the eluent. *meso*-Octamethylcalix[4]pyrrole (11 g) and *N*-confused calix[4]pyrrole (0.5 g) were isolated. The desired aldehyde (2.8 g, 62%) was obtained as a pale yellow powder, mp $>300^\circ\text{C}$. ^1H NMR (400 MHz, DMSO, δ): 1.52, 1.62 (s, 24 H, CH_3), 4.85 (d, 1 H, β -H, $J = 2.16$ Hz), 5.64, 5.72 (m, 6 H, β -H), 8.93 (s, 1 H, NH), 8.95 (s, 1 H, NH), 9.16 (s, 1 H, NH), 9.76 (s, 1 H, NH), 11.29 (s, 1 H, CHO); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, DMSO, δ): 28.1–30.3 (Me), 34.6–36.1 ($\text{C}(\text{CH}_3)_2$), 101.6–102.6 (β -pyrrole CH), 109.7 (*N*-confused pyrrole β -CH), 127.0 (*N*-confused pyrrole α -C=O), 136.8 (pyrrole α -C), 138.5–139.3 ($5 \times \alpha$ -pyrrole C), 143.9 (pyrrole β -C), 147.4 (pyrrole α -C), 178.0 (CHO); m/z (ES) 457.2960, calc. for $\text{C}_{29}\text{H}_{37}\text{N}_4\text{O}$ (MH^+) 457.2962.

N-Confused calix[4]pyrrole methylene oxoindenylidenemalonitrile **1d**

To *N*-confused calix[4]pyrrole aldehyde (0.22 mmol, 100 mg) in toluene (20 mL) was added oxoindenylidenemalonitrile (0.22 mmol, 42.7 mg) and one drop of piperidine. The mixture was heated at reflux for 3 h. The toluene was removed under reduced pressure and the residue purified using column chromatography (silica, eluent dichloromethane–ethylacetate using a gradient of 20 : 1 to 9 : 1). The product (74 mg, 53%) was obtained as a deep red powder, mp 294°C . ^1H NMR (300 MHz, CDCl_3 , δ): 1.57 (s, 12 H, Me), 1.70 (s, 6 H, Me), 1.78 (s, 6 H, Me), 4.85 (s, 1 H, *N*-confused pyrrole β -H), 5.87 (t, 6 H, pyrrole β -H), 7.25 (d, 2 H, pyrrole NH), 7.45 (s, 1 H, pyrrole NH), 7.65 (dt, 2 H, aromatic H), 7.84 (d, 1 H, aromatic H), 8.64 (d, 1 H, aromatic H), 8.68 (s, 1 H, methylene CH), 14.39 (s, 1 H, pyrrole NH); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3 , δ): 28.3–30.2 (4×2 Me), 35.2–37.4 ($4 \times \text{C}(\text{CH}_3)_2$), 66.7 ($\text{C}(\text{CN})_2$), 102.3–104.5 ($6 \times \beta$ -pyrrole CH), 115.3 (indenylidene C), 115.4 (*N*-confused pyrrole β -CH), 115.6 and 115.8 ($2 \times \text{CN}$), 123.3

(aromatic CH), 124.8 (aromatic CH) 127.7 (α -*N*-confused pyrrole $\text{C}-\text{C}=\text{C}$), 130.3 (methylene CH), 133.5 (aromatic CH), 134.7 (aromatic CH), 135.7 (α -pyrrole C), 136.7 (aromatic $\text{C}-\text{C}=\text{C}(\text{CN})_2$), 139.5 (aromatic $\text{C}-\text{C}=\text{O}$), 138.6–139.3 ($5 \times \alpha$ -pyrrole C), 155.0 (β -pyrrole C), 156.0 (α -pyrrole C), 162.4 ($\text{C}=\text{C}(\text{CN})_2$), 190.0 ($\text{C}=\text{O}$); m/z (ES) 633.3339, calc. for $\text{C}_{41}\text{H}_{41}\text{N}_6\text{O}$ (MH^+) 633.3336.

N-Confused calix[4]pyrrole methylene phenalene-1,3-dione **1e**

To *N*-confused calix[4]pyrrole aldehyde (0.22 mmol, 100 mg) in toluene (20 mL) was added phenalene-1,3-dione (0.22 mmol, 43 mg) and one drop of piperidine. The mixture was heated at reflux for 3 h. Upon cooling, the precipitate obtained was filtered (74 mg). The toluene was removed from the filtrate under reduced pressure and the residue purified using column chromatography (silica, eluent dichloromethane), a second fraction (40 mg) being isolated. The product (114 mg, 81%) was obtained as a yellow powder, mp $>300^\circ\text{C}$. ^1H NMR (300 MHz, CDCl_3 , δ): 1.58 (s, 12 H, Me), 1.74 (s, 6 H, Me), 1.85 (s, 6 H, Me), 4.93 (s, 1 H, *N*-confused pyrrole β -H), 5.95 (t, 6 H, pyrrole β -H), 7.17 and 7.29 (s, 2×1 H, pyrrole NH), 7.35 (s, 1 H, pyrrole NH), 7.73 (m, 2 H, aromatic *m*-H), 8.17 (d, 2 H, $J = 8$ Hz, aromatic *p*-H), 8.63 and 8.71 (d, 2×1 H, $J = 7$ Hz and $J = 6$ Hz, aromatic *o*-H), 9.16 (s, 1 H, methylene CH), 15.36 (s, 1 H, pyrrole NH); $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, CDCl_3 , δ): 28.8–31.5 (Me), 35.6–38.3 ($\text{C}(\text{CH}_3)_2$), 102.5–104.8 (β -CH), 115.2 (*N*-confused pyrrole β -CH), 119.2 (aromatic *o*-CH), 126.8, 127.0, 128.7, 129.6 and 133.8 (aromatic *p*-CH), 136.7 and 139.0–139.9 (α -pyrrole C), 154.1, 184.2 and 185.0 ($\text{C}=\text{O}$); m/z (ES) 635.3375, calc. for $\text{C}_{42}\text{H}_{43}\text{N}_4\text{O}_2$ (MH^+) 635.3381.

N-Confused calix[4]pyrrole methylene-1,3-dioxane-4,6-dione **1f**

To *N*-confused calix[4]pyrrole aldehyde (0.22 mmol, 100 mg) in toluene (20 mL) was added Meldrum's acid (0.22 mmol, 32 mg) and three drops of piperidine. The mixture was heated at reflux for 1 h. The toluene was removed under reduced pressure, and subsequently the crude mixture was purified using flash column chromatography (silica, eluent dichloromethane–ethyl acetate 9 : 1). The product (114 mg, 81%) was obtained as a yellow powder, mp 251°C . ^1H NMR (300 MHz, CDCl_3 , δ): 1.56–1.77 (m, 30 H, Me), 4.82 (s, 1 H, *N*-confused pyrrole β -H), 5.92 (t, 6 H, pyrrole β -H), 7.16–7.23 (m, 3 H, pyrrole NH), 8.67 (s, 1 H, methylene CH), 13.53 (s, 1 H, *N*-confused pyrrole NH); $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, CDCl_3 , δ): 27.3–29.1 (calix. Me), 31.2, 35.3, 35.4, 36.8, 37.4, 96.2, 102.3–104.5 (pyrrole β -CH), 113.9, 125.0, 136.5, 137.5, 138.8, 139.1, 139.2, 140.2, 154.7, 165.2 ($\text{C}=\text{O}$); m/z (ES) 583.3274, calc. for $\text{C}_{35}\text{H}_{43}\text{N}_4\text{O}_4$ (MH^+) 583.3279.

Crystallography

Data for **1c**, **1d** and **1f** were collected on a Bruker Nonius KappaCCD diffractometer mounted at the window of a Mo rotating anode.

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