Synthesis of monosubstituted calix[4]pyrroles in β position

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Through lithiation and electrophilic substitution of three calix[4]pyrroles, a series of new calix[4]pyrrole derivatives were synthesised. The derivatives were hydrolysed to produce acids and, under base catalysis, new esters were formed. Thus calix[4]pyrroles with an active functional group were obtained. The optimum reaction and purification conditions were investigated. The binding properties of the new derivatives with anions was examined.

Keywords: calix[4]pyrroles, macrocycles, lithiation, molecular recognition, supramolecular chemistry

Calix[4]pyrroles, known as good receptors for anions and neutral substrates, are macrocyclic species composed of four pyrrole rings linked in the α-position *via* sp^3-hybridised carbon atoms. They have been used as colourimetric[1,2] and electrochemical[3] sensors, new solid supports of LC,[4] *etc.* The syntheses of new receptors derived from calix[4]pyrroles are a challenge in calixpyrrole chemistry.[5,6] Up to now, derivatisation of calix[4]pyrroles is mainly in the *meso*-position, β-position and *N*-position,[7] in which all the reactions keep the skeleton of calix[4]pyrroles. Expansion of the polypyrrolic ring or addition of other chemical groups on the polypyrrolic ring have also made great progresses.[8,9]

In this paper, through the lithiation of calix[4]pyrroles and the subsequent electrophilic substitution, some interesting new monosubstituted calix[4]pyrrole derivatives were obtained. They not only showed some potential properties as host molecules but were also important precursors for the construction of many new receptors and LC solid support. The synthetic procedure[10-12] in Scheme 1 was used.

Structural formulas of the products are listed in Fig. 1.

Results and discussion

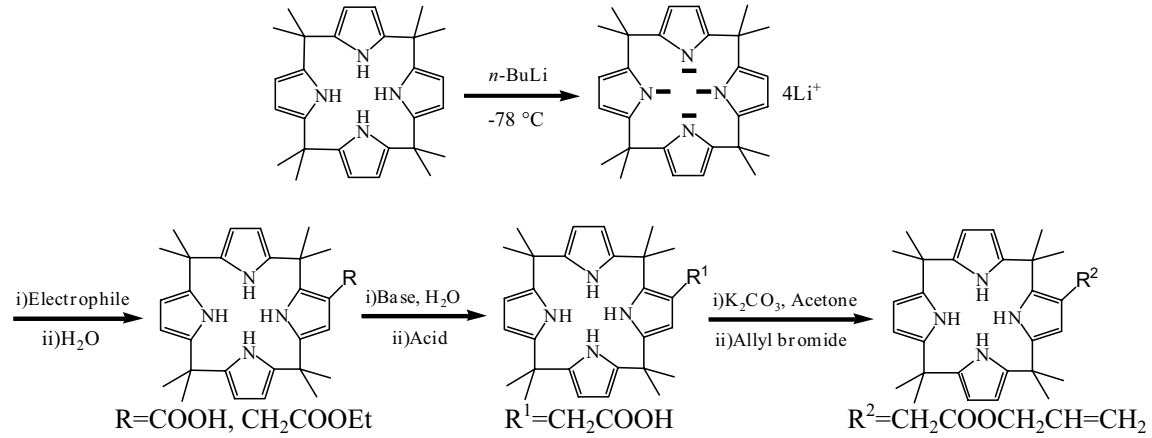
Effect of the equivalents of ethyl bromoacetate on the yields of calix[4]pyrrole monoesters

The optimum quantities of ethyl bromoacetate added as the electrophile were different for the three starting calix[4]pyrroles in order to obtain the highest yields of the calix[4]pyrrole monoesters. Figure 2 shows the effect of increasing the amount of ethyl bromoacetate on the yield of mono- and disubstituted *meso*-tetraspirocyclopentylcalix[4]pyrrole, in which the maximum yield of the monosubstituted product (21%) is obtained using 4 equivalents of ethyl bromoacetate. For *meso*-octamethylcalix[4]pyrrole, it is 3 equivalents and for *meso*-tetraspirocyclohexylcalix[4]pyrrole, it is 4.5 equivalents. In addition, under optimised conditions, the yield of **4** is greater than **5** or **6**, which is attributed to the stronger spatial hindrance of the cyclopentyl or cyclohexyl groups in the *meso*-position compared with a methyl group.

Binding affinities of monosubstituted derivatives with anions

The stability constants of monosubstituted products with anions were measured by spectral titration under Benisi–Hilderberg conditions,[13] which provided the base for understanding the binding properties between host and guest molecules. Figures 3 and 4 are the absorption spectra of *meso*-tetraspirocyclopentylcalix[4]pyrrole and **6** in EtOH after adding different equivalents of tetramethylammonium chloride. The concentrations of the host molecules were fixed at 5×10^{-5} M and 2×10^{-5} M, respectively. Some stability constants of tetraspirocyclopentylcalix[4]pyrrole and its monosubstituted derivative **6** with anionic substrates are listed in Table 1 for comparison.

From Table 1, it can be seen that the binding ability of monosubtituted product **6** decreases in the order of F^-, Cl^- and Br^-, which is similar to that of its predecessor. Other monosubtituted products have similar results. All these revealed the potential recognition ability of monosubstituted derivates to anions. From Table 1, we also find that with the same anion, the stability constant of **6** is lower than that of *meso*-tetraspirocyclopentylcalix[4]pyrrole, which may be due to the unfavourable interaction between the bound anion and the lone pair electrons on the oxygen atoms of the ester group.[11]



Scheme 1 Synthetic procedure.

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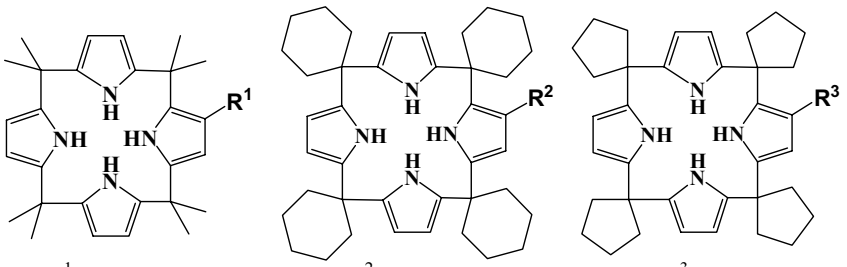

1 R^1=COOH **2** R^2=COOH **3** R^3=COOH
4 R^1=CH_2COOEt **5** R^2= CH_2COOEt **6** R^3= CH_2COOEt
7 R^1=CH_2COOH **8** R^2= CH_2COOH **9** R^3= CH_2COOH
10 R^1=$CH_2COOCH_2CH{=}CH_2$

Fig. 1 Structural formulas of monosubstituted products of calix[4]pyrroles.

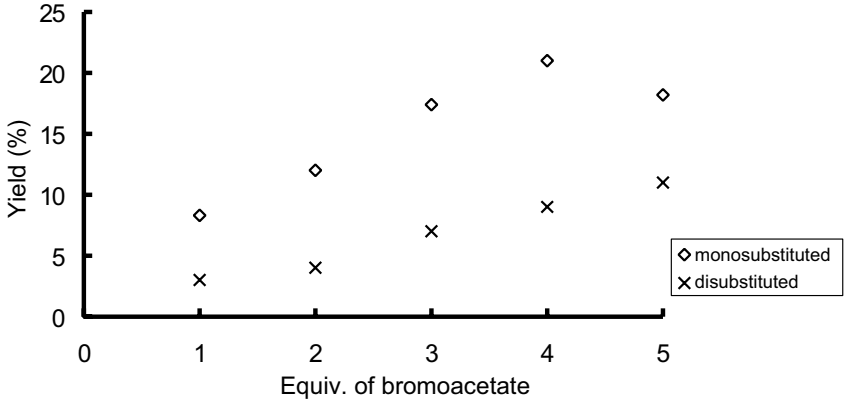

Fig. 2 Yields of mono- and disubstituted esters of *meso*-tetraspirocyclopentylcalix[4]pyrrole with different amounts of ethyl bromoacetate.

Experimental

General procedures

Instruments used for the characterisation of products were a Nicolet 10 DX FT-IR infrared spectrophotometer in KBr pellet, a Varian INOVA-400 FT-NMR (TMS used as the internal standard), a VG ZAB-HS mass spectrometer and a Perkin Elmer Lambda 35 UV-VIS spectrometer. The TLC sheets used were DC-Alufolien 60 Å neutral aluminium sheets (Merck, Germany, with a layer thickness of 0.2 mm). Column chromatography was carried out on Al_2O_3 (mesh 100–200).

n-Butyllithium in hexane (2.6 M) was purchased from Fluka. Other chemicals and reagents were purchased in China and were of A. R. grade.

The starting materials, *meso*-octamethylcalix[4]pyrrole, *meso*-tetraspirocyclopentylcalix[4]pyrrole and *meso*-tetraspirocyclohexylcalix[4]pyrrole, were synthesised[14-16] in our laboratory.

Lithiation of the starting calix[4]pyrroles: The starting calix 4]pyrroles (4–5 g) was dissolved in dry THF (250 ml) and cooled to –78 °C under argon atmosphere. *n*-Butyllithium of 4 equiv. of the starting calix[4]pyrroles in hexane was added dropwise to THF solution with stirring. After the addition was finished, the reaction mixture was kept in –78°C with stirring for another 30 min and directly used in the next step.

Synthesis of calix[4]pyrrole-β-formic acids: An excess of dry ice was added quickly to the reaction solution and kept in –78°C for 12 h. THF was then removed *in vacuo*. The residue was suspended in water (300 ml) with stirring for 30 min. The deposit was removed by centrifugation. The solution left was stirred and acidified by adding aqueous perchloric acid or sulfuric acid (35 %) dropwise until pH value was between 1 and 2 (tested by indicator paper). The white precipitate appeared was separated again by centrifugation and then dissolved into dichloromethane (25 ml). The trace water was removed by magnesium sulfate. After centrifugation, the solvent was removed *in vacuo* and the residue was crystallised in acetone/water by slow evaporation. After dryness, a white monoformic acid was acquired.

Yield: Acid **1** ($C_{29}H_{36}N_4O_2$) was 8 % (0.35 g product from 4.00 g raw material), m. p. 193–194°C. ^{1}H NMR (400 M, DMSO-d_6) δ 11.50 (s, 1H, CO_2H), 9.87 (s, 2H, NH), 8.90 (s, 1H, NH), 8.24 (s, 1H, NH), 6.15 (m, 1H, pyrrole CH), 5.93 (m, 2H, pyrrole CH), 5.65 (m,

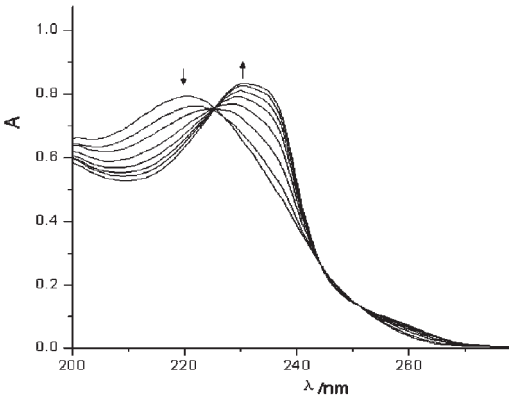

Fig. 3 Absorption spectra of tetraspirocyclopentyl calix[4] pyrrole recorded in EtOH (5×10^{-5}M) before and after the addition of 8, 16, 24, 32, 4 0,48, 56 and 64 equivalents of tetramethylammonium chloride.

Table 1 Stability constants for TCP calix[4]pyrrole[a] and its monosubstituted derivative **6** with anionic substrates

Anion[b]	Stability constants[c]/mol/l	
	TCP Calix[4]pyrrole	Compound **6**
F^-	2.2×10^3	1.7×10^3
Cl^-	2.7×10^2	2.4×10^2
Br^-	1.6×10^2	1.5×10^2

[a]TCP calix[4]pyrrole was *meso*-tetraspirocyclopentylcalix[4] pyrrole.
[b]Anions were their tetramethylammonium salts.
[c]Anions were added as the tetramethylammonium salt to EtOH solutions of the receptor. After equilibrating for 24 h at 20°C, the absorption spectra of the solutions were recorded.

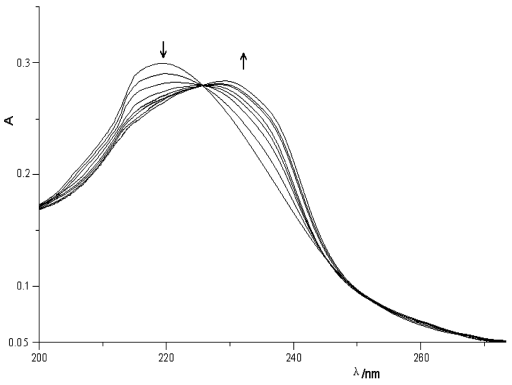

Fig. 4 Absorption spectra of compound **6** recorded in EtOH (2×10^{-5}M) before and after the addition of 10, 30, 50, 70, 90, 110 and 130 equivalents of tetramethylammonium chloride.

2H, pyrrole CH), 5.59 (m, 2H, pyrrole CH), 1.68 (s, 6H, CCH_3), 1.53 (s, 6H, CCH_3), 1.50 (s, 12H, CCH_3); IR, ν/cm^{-1} (KBr pellet) 3412 (s), 3110 (w), 2969 (s), 1702 (s), 1237 (s), 1030 (s), 771 (s); Anal. Calcd for $C_{29}H_{36}N_4O_2$: C, 73.70 %; H, 7.68 %; N, 11.85 %. Found: C, 73.74 %; H, 7.61 %; N, 11.93 %; MS (FAB + , *m/z*): 472 (M^+, 38), 457 (M-CH_3, 29), 441 (M-2CH_3, 7).

Acid **2** ($C_{41}H_{52}N_4O_2$) was 4 % (0.24 g product from 5.50 g raw material), m.p. 175–176°C. ^{1}H NMR (400 M, $CDCl_3$) δ 7.42 (s, 1H, NH), 7.36 (s, 1H, NH), 7.06 (s, 1H, NH), 6.51 (s, 1H, NH), 6.08–5.80 (m, 7H, pyrroleCH), 2.17 (s, 10H, CH_2), 1.91 (s, 10H, CH_2), 1.49 (m, 20H, CH_2); IR,ν/cm^{-1} (KBr pellet) 3419 (s), 3104 (w), 2933 (s), 2854 (s), 1720 (s), 1572 (m), 1437 (s), 1191 (s), 766 (s); Anal. Calcd for $C_{41}H_{52}N_4O_2$: C, 77.81 %; H, 8.28 %; N, 8.85 %. Found: C, 77.75 %; H, 8.24 %; N, 8.89 %; MS (FAB + , *m/z*): 632 (M^+, 52).

Acid **3** ($C_{37}H_{44}N_4O_2$) was 5 % (0.27 g product from 4.97 g raw material), m.p. 166–167°C. ^{1}H NMR (400 MHz, $CDCl_3$), δ 7.52 (s, 1H, NH), 7.40 (s, 1H, NH), 7.02 (s, 1H, NH), 6.46 (s, 1H, NH), 6.04–5.77 (m, 7H, pyrroleCH), 2.17 (s, 8H, CH_2), 2.08 (s, 8H, CH_2), 1.67 (m, 16H, CH_2); IR,ν/cm^{-1} (KBr pellet) 3421 (s), 3106 (w), 2964 (s), 2862 (s), 1731 (s), 1563 (m), 1174 (s), 1036 (s), 766 (s); Anal. Calcd for $C_{37}H_{44}N_4O_2$: C, 77.05 %; H, 7.69 %; N, 9.71 %. Found: C, 77.14 %; H, 7.76.24 %; N, 9.78 %; MS (FAB + , *m/z*): 576 (M^+, 61).

Synthesis of meso-octamethylcalix[4]pyrrole-β-ethyl acetate **4**: 3 equiv. of ethyl bromoacetate to was added dropwise to the stirred lithiation solution of *meso*-octamethylcalix[4]pyrrole at –78°C and the resulting kept for 2 h. After warming to room temperature, the mixture was kept stirring for another 2 h. Then THF was removed *in vacuo*. The residue was dissolved in EtOH (100 ml) and the solution was stirred vigorously. Water (100 ml) was added slowly and a white deposit appeared. After centrifugation, the precipitate was dried under high vacuum. The monoester was then purified on a Al_2O_3 column, the eluent used was hexane/dichloromethane (3: 1). The second fraction (R_f = 0.31) was monoester **4**.

Monoester **4** was recrystallised from EtOH to give a pure product with a yield of 41 % (1.97 g monoester from 4.00 g raw material), m.p. 181–182°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.51 (s, 1H, NH), 7.17 (s, 1H, NH), 6.98 (s, 1H, NH), 6.95 (s, 1H, NH), 5.92–5.85 (m, 5H, pyrrole CH), 5.79 (s, 1H, pyrrole CH), 5.69 (s, 1H, pyrrole CH), 4.20 (q, 2H, *J* = 7.2 Hz, ethyl CH_2), 3.62 (s, 2H, CCH_2), 1.63–1.47 (overlapping singlets, 24H, CCH_3), 1.30 (t, 3H, *J* = 7.2 Hz, ethyl CH_3); IR,ν/cm^{-1} (KBr pellet) 3439 (s), 3344 (s), 3103 (w), 2970 (s), 1724 (s), 1410 (s), 1333 (s), 1201 (s), 1044 (m), 761 (s); Anal. Calcd for $C_{32}H_{42}N_4O_2$: C, 74.67 %; H, 8.22 %; N, 10.88 %. Found: C, 74.58 %; H, 8.29 %; N, 10.78 %; MS (FAB + , *m/z*): 514 (M^+, 37), 499 (M-CH_3, 34), 482 (M-2CH_3, 6), 441 (M-C_2H_5OCO, 8).

Synthesis of ethyl meso-tetraspirocyclohexylcalix[4]pyrrole-β-acetate **5**: The method used was similar to that of **4,** but 4 equivalents of ethyl bromoacetate were used. The eluent was hexane/dichloromethane (4.5: 1). The second fraction (R_f = 0.34) was monoester **5**.

Monoester **5** was recrystallised from acetone or EtOH to give a pure product with a yield of 19 % (1.20 g monoester from 5.50 g raw material), m.p. 133–134°C; ^{1}H NMR (400 MHz, $CDCL_3$) δ 8.19 (s, 1H, NH), 7.08 (s, 1H, NH), 7.03 (s, 1H, NH), 7.02 (s, 1H, NH), 5.91–5.83 (m, 5H, pyrrole CH), 5.72 (s, 1H, pyrrole CH), 5.71 (s, 1H, pyrrole CH), 4.22–4.17 (q, 2H, *J* = 7.2 Hz, ethyl CH_2), 3.58 (s, 2H, CCH_2), 2.01–1.84 (m, 16H, CH_2), 1.60–1.51 (m, 24H, CH_2), 1.36 (t, 3H, *J* = 7.6 Hz, ethyl CH_3); IR,ν/cm^{-1} (KBr pellet) 3405 (s), 3349 (s), 3105 (w), 2930 (s), 2855 (s), 1721 (s), 1576 (m), 1447 (s), 1183 (s), 1045 (s), 765 (s); Anal. Calcd for $C_{44}H_{58}N_4O_2$: C, 78.30 %; H, 8.66 %; N, 8.30 %. Found: C, 78.37 %; H, 8.58 %; N, 8.35 %; MS (FAB +, *m/z*): 674 (M^+, 38), 601 (M-CH_3CH_2OCO, 7).

Synthesis of ethyl meso-tetraspirocyclopentylcalix[4]pyrrole-β-acetate **6**: The method used was similar to that of **4,** but the 4 equivalents of ethyl bromoacetate were used. The eluent of column was hexane/dichloromethane (4: 1). The second fraction (R_f = 0.38) was monoester **6**.

Monoester **6** was recrystallised from acetone or EtOH to give a pure product with a yield of 21 % (1.21 g monoester from 4.97 g raw material), m.p. 97–98°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.62 (s, 1H, NH), 7.13 (s, 1H, NH), 7.00 (s, 1H, NH), 6.98 (s, 1H, NH), 5.87–5.80 (m, 5H, pyrroleCH), 5.73 (s, 1H, pyrroleCH), 5.65 (m, 1H, pyrrole CH), 4.20 (q, 2H, *J* = 7.2 Hz, ethylCH_2), 3.58 (s, 2H, CCH_2), 2.11–1.97 (t, 16H, CH_2), 1.70–1.55 (m, 16H, CH_2), 1.32 (t, 3H, *J* = 7.2 Hz, ethyl CH_3); IR, ν/cm^{-1} (KBr pellet) 3418 (s), 3342 (w), 3105 (w), 2957 (s), 2871 (s), 1725 (s), 1578 (m), 1454 (s), 1182 (s), 1041 (s), 764 (s); Anal. Calcd for C $_{40}H_{50}N_4O_2$: C, 77.63 %; H, 8.14 %; N, 9.05 %. Found: C, 77.57 %; H, 8.19 %; N, 9.11 %; MS (FAB + , *m/z*): 618 (M^+, 38).

Syntheses of ethyl esters of monoacids **7**, **8** *and* **9**: 0.423 mmol of monoester was dissolved in EtOH (20 ml) and refluxed. Sodium hydroxide (24 ml, 2.0 M) was added slowly with stirring. The resulting mixture was refluxed for 6 h. After cooled to room temperature, EtOH was removed *in vacuo*. The solution was then acidified with perchloric acid or sulfuric acid (35 %) to pH 1–2 (measured by indicator paper) and kept for 6 h. 50 ml of dichloromethane was added to extract product. Then the organic layer was separated and extracted by 100 ml water again. After separation, magnesium sulfate was added to the organic layer to get rid of the trace water. After centrifugation, hexane (50 ml) was added slowly into the solution and a white product was obtained. After filtration, the product was dried under vacuum.

meso-Octamethylcalix[4]pyrrole-β-acetic acid **7** *($C_{30}H_{38}N_4O_2$)*: M.p. 145–146°C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.97 (s, 1H, CO_2H), 9.34 (s, 1H, NH), 9.19 (s, 1H, NH), 8.75 (s, 1H, NH), 8.29 (s, 1H, NH), 5.76–5.66 (m, 5H, pyrrole CH), 5.63 (s, 1H, pyrrole CH), 5.55 (s, 1H, pyrrole CH), 3.39 (s, 2H, CCH_2), 1.53 (s, 6H, CCH_3), 1.48 (s, 12H, CCH_3), 1.43 (s, 6H, CCH_3); IR,ν/cm^{-1} (KBr pellet) 3428 (s), 3108 (w), 2968 (s), 1702 (s), 1234 (s), 1043 (w), 769 (s); Anal. Calcd for $C_{30}H_{38}N_4O_2$: C, 74.04 %; H, 7.87 %; N, 11.51 %. Found: C, 74.12 %; H, 7.81 %; N, 11.56 %; MS (FAB + , *m/z*): 486 (M^+, 55), 471 (M-CH_3, 28), 441 (M-COOH, 22).

meso-Tetraspirocyclohexylcalix[4]pyrrole-β-acetic acid **8** *($C_{42}H_{54}N_4O_2$)*: M.p. 212–213°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (s, 1H, NH), 7.19 (s, 1H, NH), 7.01 (s, 1H, NH), 6.97 (s, 1H, NH), 5.94–5.85 (m, 5H, pyrrole CH), 5.77 (m, 1H, pyrrole CH), 5.75 (m, 1H, pyrrole CH), 3.66 (s, 2H, CCH_2), 2.24 (s, 10H, CH_2), 1.96 (s, 10H, CH_2), 1.50–1.43 (m, 20H, CH_2); IR, ν/cm^{-1} (KBr pellet) 3407 (s), 3104 (w), 2938 (s), 2858 (s), 1720 (s), 1574 (m), 1440 (s), 1190 (s), 762 (s); Anal. Calcd for $C_{42}H_{54}N_4O_2$: C, 77.98 %; H, 8.41 %; N, 8.66 %. Found: C, 77.91 %; H, 8.47 %; N, 8.58 %; MS (FAB + , *m/z*): 646 (M^+, 42), 601 (M-COOH, 18), 587 (M-CH_2COOH, 7).

meso-Tetraspirocyclopentylcalix[4]pyrrole-β-acetic acid **9** *($C_{38}H_{46}N_4O_2$)*: M.p. 197–198°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (s, 1H, NH), 7.08 (s, 1H, NH), 7.03 (s, 1H, NH), 6.98 (s, 1H, NH), 5.87–5.81 (m, 5H, pyrrole CH), 5.76 (m, 1H, pyrrole CH), 5.40 (m, 1H, pyrrole CH), 3.65 (s, 2H, CCH_2), 2.16–1.99 (m, 16H, CH_2), 1.68 (s, 16H, CH_2); IR,ν/cm^{-1} (KBr pellet) 3422 (s), 3107 (w), 2956 (s), 2862 (s), 1722 (s), 1577 (m), 1450 (s), 1185 (s), 764 (s); Anal. Calcd for $C_{38}H_{46}N_4O_2$: C, 77.25 %; H, 7.85 %; N, 9.48 %. Found: C, 77.18 %; H, 7.76 %; N, 9.42 %; MS (FAB + , *m/z*): 590 (M^+, 26), 545 (M-COOH, 22).

Synthesis of allyl meso-octamethylcalix[4]pyrrole-β-acetate **10**: 150 mg (0.31 mmol) of *meso*-octamethylcalix[4]pyrrole-β-acetic acid **7** was dissolved in dry acetone (20 ml), 0.213 g of potassium carbonate was added with stirring. Then the solution was refluxed under argon atmosphere for 1 h. After cooled to room temperature, 0.0225 ml (0.31 mmol) of allyl bromide was added to the solution dropwise and 0.009 g of tetrabutylammonium iodine was also added. The resulting mixture was refluxed under argon atmosphere for 24 h. The solvent was removed *in vacuo* and then the residue was dissolved in ethanol. After centrifugation, ethanol was removed in vacuum and 154 mg of white product **10** was obtained with a yield of 95 %.

Allyl meso-Octamethylcalix[4]pyrrole-β-acetate **10** *($C_{33}H_{42}N_4O_2$)*: M.p. 124–125°C; ^{1}H NMR (400 MHz, $CDCl_3$), δ 8.44 (s, 1H, NH), 7.34 (s, 1H, NH), 7.00 (s, 1H, NH), 6.97 (s, 1H, NH), 5.91–5.86 (m, 6H, 5

pyrrole CH + CH_{hook}), 5.80 (m, 1H, pyrrole CH), 5.70 (m, 1H, pyrrole CH), 5.26 (d, 2H, J = 9.6 Hz, $CH_{2end\ of\ hook}$), 4.64 (d, 2H, J = 6.0 Hz, OCH_2), 3.66 (s, 2H, CCH_2), 1.71–1.47 (singlets, 24H, CCH_3); IR, ν/cm^{-1} (KBr pellet) 3440 (s), 3348 (s), 3104 (s), 2969 (s), 1725 (s), 1666 (s), 1410 (s), 1181 (m), 988 (m), 761 (s); Anal. Calcd for $C_{33}H_{42}N_4O_2$: C, 75.25 %; H, 8.04 %; N, 10.64 %. Found: C, 75.32 %; H, 8.09 %; N, 10.57 %; MS (FAB + , *m/z*): 526 (M^+, 43), 511 (M-CH_3, 36), 499 (M-C_2H_3, 13), 441 (M-C_3H_5OCO, 8).

Conclusions

A synthetic method for monosubstituted calix[4]pyrrole derivatives in β-position was established. It opened a wide field for the synthesis and further applications of new calix[4]pyrroles. The optimum conditions for reactions and purification were determined. The binding properties of the new synthesised derivatives with anions were discussed. At present, further studies on these products are in progress.

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References

1 S.J. Shao, Y. Guo, L.J. He, S.X. Jiang and X.D. Yu, *Tetrahedron Lett.*, 2003, **44**, 2175.
2 H. Miyaji, W. Sato and J.L. Sessler, *Angew. Chem. Int. Ed.*, 2000, **39**, 1777.
3 K.A. Nielsen, J.O. Jeppesen, E. Levillain and J. Becher, *Angew. Chem. Int. Ed.*, 2003, **42**,187.
4 J.L. Sessler, P.A. Gale and J.W. Genge, *Chem. Eur. J.* 1998, **4**, 1095.
5 C.N. Warriner, P.A. Gale and M.E. Light, *Chem. Commun.*, 2003, **12**, 1810.
6 J.L. Sessler, V. Kral, T.V. Shishkanova and P.A. Gale, *Proc. Nat. Acad. Sci*., 2002, **99**, 4848.
7 J.L. Sessler, S. Camiolo and P.A. Gale, *Coord. Chem. Rev.*, 2003, **240**,17.
8 E.C. Lee, Y.K. Park, J.H. Kim, H. Hwang, Y.R. Kim and C.H. Lee, *Tetrahedron Lett.*, 2002, **43**,9493.
9 A. Nagarajan, J.W. Ka and C.H. Lee, *Tetrahedron*, 2001, **51**, 7323.
10 Jr. Pavel Anzenbacher, J. Karolina, J.A. Shriver, H. Miyaji, V.M. Lynch, J.L. Sessler and P.A. Gale, *J. Org. Chem.*, 2000, **65**, 7641.
11 P.A. Gale, J.L. Sessler, W.E. Allen, N.A. Tvermoes and V. Lynch, *Chem. Commun.*, 1997, 665.
12 J.L. Sessler, A. Andrievsky, P.A. Gale and V. Lynch, *Angew. Chem. Int. Ed. Engl.*, 1996, **35**, 2782.
13 H.A. Benesi and J.H. Hildebrand, *J. Am. Chem. Soc.*, 1949, **71**, 2703.
14 S.J. Shao, X.D. Yu and S.Q. Cao, *Chin. Chem. Lett.*, 1999, **10**, 193.
15 W.H. Brown and B.J. Hutchinson, M.H. Mackinnon, *Can. J. Chem.*, 1971, **49**, 4017.
16 B.J. Littler, M.A. Miller, C.H. Hung, R.W. Wagner, D.F. O'Shea, P.D. Boyle and J.S. Lindsey, *J. Org. Chem.*, 1999, **64**,1391.