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5-Methyl-5-aryldipyrromethanes: synthesis, crystal structure and anion binding studies

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The eco-friendly and selective syntheses of 5-methyl-5-aryldipyrromethanes (**1**–**4**) in which aryl is FC_6H_4 **1**, ClC_6H_5 **2**, $CH_3OC_6H_5$ **3** and $CH_3C_6H_5$ **4**, have been reported in the presence of citric acid (weak organic acid) and characterised by IR, ^{1}H NMR, ^{13}C NMR and mass spectroscopy. The structures of **2**–**4** have been confirmed by X-ray crystallography. Anion binding studies of **1**–**4** with different anions (e.g. F^-, Cl^-, CH_3COO^-, $H_2PO_4^-$ and HSO_4^-) have been carried out by ^{1}H NMR titrations and binding constants have been evaluated using EQNMR program, revealing that they bind fluoride selectively compared with other anions with 1:1 stoichiometry in $CDCl_3$. The binding affinities of these compounds are influenced by the nature of the substituent on the *meso*-carbon atom.

Keywords: methylaryldipyrromethanes; crystal structure; anion recognition; ^{1}H NMR titrations

Introduction

Dipyrromethanes interact with anions through H-bonding because of acidic character of NH protons, although their molecular recognition chemistry has been less explored as compared with calix[4]pyrroles (*1*). Anion sensing and neutral molecules sensing have been reported only for a few dipyrromethanes and its derivatives (*2*). Charge-transfer complex consisting of dihydroxymethyldi-(2-pyrrolyl)methane and tetracyanoquinodimethane selectively distinguishes cysteine from other amino acids which also proved as a colorimetric probe for aniline. Similar types of charge-transfer complexes have also been reported to show excellent selectivity for other inorganic anions (*3*).

Introduction of electron-withdrawing compared with that of electron-releasing groups in dipyrromethanes (*4*) and calix[4]pyrroles (*5*) skeleton increases the acidity of pyrrolic protons which in turn enhances their affinity and selectivity towards anions. Introduction of bulky groups such as admantane at *meso*-carbons also resulted in enhanced association constants for anions (e.g. F^-, Cl^-, Br^-, HSO_4^- and $H_2PO_4^-$) because of hindered rotational mobility of pyrrole moieties (*2*).

The binding constants (1:1) with fluoride ion for various dipyrromethanes follow the order dimethyldipyrromethanes (*6*) > phenyldipyrromethanes (*2a*) > diphenyldipyrromethanes (*4a*). The observed order may be due to stronger repulsive interactions between the anion and the two aryl rings. In general, dipyrromethanes are more selective towards fluoride ion forming both 2:1 (host:fluoride) and 1:1 complexes rather than other anions (e.g. chloride, bromide, acetate, nitrate, hydrogen sulphate and dihydrogen phosphate) forming 1:1 complexes (*2a,b*). Molecular recognition of anions, cations and neutral molecules by various receptors (*7*) are biomimetic processes (*8*) and is a remarkable achievement in the field of supramolecular chemistry.

Dipyrromethanes are the precursors for the synthesis of porphyrins, calix[4]phyrins, corroles, calix[4]pyrroles and phlorins (*9*) that have a wide variety of applications in the fields of medicine, material science and optical sensors (*10*). Dipyrromethanes are generally synthesised by acid-catalysed condensation of aldehydes or ketones in the presence of excess of pyrrole. Chemists are now trying to develop more efficient and eco-friendly methods to synthesise compounds by using milder acids as catalyst and eco-friendly solvents as compared with traditional acid-catalysed condensation reactions of aldehydes or ketones with excess pyrrole as solvent (*11*).

The strength of our pathway is the use of non-hazardous, inexpensive weak organic acid and green solvent, i.e. water, leading to good yields of products by recrystallisation. This method avoids excess use of reactant, i.e. pyrrole, and also limits the formation of oligomeric and polymeric products. To the best of our knowledge, the chemistry of *meso*-methylaryldipyrromethanes is not well established, and they could be potential receptors as well as good building blocks for the synthesis of *meso*-functionalised calix[4]pyrroles. Among methylaryldipyrromethanes, binding studies of only 5-methyl-5(4-nitrophenyl)dipyrromethane and its further use as precursor for the synthesis of *meso*-functionalised and expanded calix[4]pyrroles have been reported in the

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literature (*6*). In this work, we report syntheses of 5-methyl-5-aryldipyrromethanes **1–4**, study of their anion binding properties and crystal structure of **2–4**. It is anticipated that the presence of electron-withdrawing group in **1** and **2** would enhance the anion binding ability than electron-releasing groups in **3** and **4** at the *para*-position of *meso*-phenyl substituents.

Experimental

General information

Melting points were determined on Gallenkamp electrically heated apparatus in open capillaries and were uncorrected. ^{1}H and ^{13}C NMR were recorded in $CDCl_3$ on the FT NMR Spectrometer model Avance-II 400 (Bruker UK Limited, Banner Lane, Coventry, CV4 9GH) using tetramethylsilane as internal standard, and chemical shifts are expressed in ppm. FT-IR spectra were recorded on the FT PerkinElmer RX I-FTIR Spectrophotometer using KBr (solid) as medium and expressed in cm^{-1}. Mass spectra were recorded on Waters micromass Q_TOF Micro^{TM}. X-ray crystallographic data were collected on 'Bruker APEX-II CCD' area detector diffractometer using graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) source. The crystal structures were solved by direct method using the SIR-97 program and refined by full-matrix least-squares refinement methods based on F^2, using SHELXLT-PC program (*12d*). All the CH hydrogens were attached geometrically. Molecular structures of compounds were drawn with the help of Oak Ridge Thermal Ellipsoid Plot (ORTEP) program. Hydrogen bonding was calculated using PARST (*12*). Pyrrole and ketones were distilled immediately prior to use.

Representative experimental procedure for the synthesis 5-methyl-5-(4-fluorophenyl)dipyrromethane 1

4-Fluoroacetophenone, 1.21 ml (0.01 mol), and citric acid (1%, w/v) were dissolved in distilled water (30 ml). Pyrrole, 1.38 ml (0.02 mol), was added dropwise to this solution with a constant stirring. The reaction mixture was refluxed till the reaction was complete. The reaction was quenched by adding 10 ml of 1 M ammonia solution leading to separation of product as a sticky mass. The crude was thoroughly washed with water to remove any unreacted reagents. Finally, it was recrystallised by dissolving in methanol:water (1:1). A single spot on the Thin Layer Chromatography (TLC) plate for each of these compounds confirmed the presence of one compound in each case.

*Synthesis of **2–4***: Compounds **2–4** were also synthesised using a similar procedure.

Representative experimental procedure for the synthesis tetra-cyclohexylcalix[4]pyrrole 5

A mixture of 5.8 ml of acetone (0.1 mol), 0.69 ml of pyrrole (0.01 mol) and weak organic acid (10.0%) was refluxed for 4.0 h in a round-bottomed flask. The reaction was quenched by adding ammonia solution. Then, the product separated out as sticky mass which was thoroughly washed with water to remove any unreacted pyrrole, ketone and weak acid. Finally, it was recrystallised by dissolving in acetone/methanol. A single spot on the TLC plate for each of these compounds confirmed the presence of one compound in each case.

*Synthesis of **6–8***: Compounds **6–8** were also synthesised using a similar procedure.

Anion binding studies

^{1}H NMR titrations: ^{1}H NMR titrations were carried out by the addition of Bu_4NF (1 M) or Bu_4NCl (1 M) to 0.0045 M solution of **1–4** in $CDCl_3$ solvent. After each addition, NMR spectrum was recorded. The association constants were determined by fitting the dependence of the chemical shift of the NH signal ($\Delta\delta$) to the anion concentration, using the EQNMR program.

Spectral data of 1–4

*Compound **1***: 55%; light brown solid, mp 83°C; ^{1}H NMR ($CDCl_3$, 400 MHz, ppm) δ 1.9 (s, 3H, CH_3), 5.8 (m, 2H, pyrrole-H$^{\alpha'}$), 6.0 (m, 2H, pyrrole-H$^{\beta'}$), 6.5 (m, 2H, pyrrole-H$^{\beta}$), 6.8 (m, 2H, Ph-H), 6.9 (m, 2H, Ph-H), 7.6 (br, s, 2H, NH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 29.7 (C, CH_3), 44.3 (C, *meso*), 106.5 (β'-C, pyrrole), 108.3 (β-C, pyrrole), 117.2 (α'-C, pyrrole), 137.2 (α-C, pyrrole), 129.1, 114.9 (Ph-C), 143.2 (Ph-C), 162.7 (Ph-C); IR (KBr): ν 3416.5 (pyrrole NH), 3102.2 (β-pyrrole C–H), 2979.0, 1901.6, 1668.5, 1598.5, 1553.2, 1505.7, 1463.4, 1415.6, 1400.6, 1300.8, 1264.7, 1222.6, 1162.2, 842.5. 776.8 and 721.6 cm^{-1}; MS(EI) *m/z*: 254.1 (M^+), 240.1 (M^+-CH_3), 188.1 (100%) (M-pyrrole), 121.0 (M^+-2 pyrrole).

*Compound **2***: 65%; light brown solid, mp 85°C; ^{1}H NMR ($CDCl_3$, 400 MHz, ppm) δ 2.0 (s, 3H, CH_3), 5.9 (m, 2H, pyrrole-H$^{\alpha'}$), 6.2 (m, 2H, pyrrole-H$^{\beta'}$), 6.7 (m, 2H, pyrrole-H$^{\beta}$), 7.05–7.08 (m, 2H, Ph-H), 7.24–7.28 (m, 2H, Ph-H), 7.8 (br, s, 2H, NH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 28.8 (C, CH_3), 44.4 (C, *meso*), 106.5 (β'-C, pyrrole), 108.3 (β-C, pyrrole), 117.2 (α'-C, pyrrole), 136.9 (α-C, pyrrole), 129.8, 128.2 (Ph-C), 132.5 (Ph-C), 146.0 (Ph-C); IR (KBr): ν 3430.9 (pyrrole NH), 3099.8 (β-pyrrole C–H), 2980.09, 1664.78, 1572.3, 1553.39, 1485.68, 1303.3, 1128.04, 1090.1, 1026.5, 882.1, 837.5, 791.7 and 718.6 cm^{-1}; MS(EI) *m/z*: 269.1($M^+ - 1$), 204.1 (100%) (M^+-pyrrole), 137.0 (M^+-2 C_4H_4N).

*Compound **3***: 55%; colourless crystals, mp 125°C; ^{1}H NMR ($CDCl_3$, 400 MHz, ppm) δ 2.0 (s, 3H, CH_3), 3.78 (s, 3H, OCH_3), 5.9 (m, 2H, pyrrole-H$^{\alpha'}$), 6.1 (m, 2H, pyrrole-H$^{\beta'}$), 6.6 (m, 2H, pyrrole-H$^{\beta}$), 6.7–6.8 (m, 2H, Ph-H), 7.01–7.03 (m, 2H, Ph-H), 7.7 (br, s, 2H, NH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 29.0 (CH_3), 44.1 (*meso*, C), 55.32

(OCH_3, C), 106.2 (β′-C, pyrrole), 108.2 (β-C, pyrrole), 113.4 (α′-C, pyrrole), 137.8 (α-C, pyrrole), 128.5, 116.9 (Ph-C), 139.5 (Ph-C), 158.2 (Ph-C); IR (KBr): ν 3410.4 (pyrrole NH), 3051.7 (β-pyrrole C–H), 3099.8, 2905.6, 2835.3 1602.9, 1580.9, 1557.4, 1457.7, 1373.9, 1242.7, 1115.3, 1066.3, 1025.0, 794.8, 772.7 and 713.2 cm^{-1}; MS(EI) *m/z*: 200.1(100%) (M-pyrrole), 185.1 (M-CH_3-pyrrole), 133.1 (M-2 pyrrole).

Compound ***4***: 58%; colourless crystals, mp 120°C; ^{1}H NMR ($CDCl_3$, 400 MHz, ppm) δ 2.2 (s, 3H, CH_3), 1.9 (s, 3H, CH3), 5.8 (m, 2H, pyrrole-$H^{\alpha'}$), 6.0 (m, 2H, pyrrole-$H^{\beta'}$), 6.5 (m, 2H, pyrrole-H^{β}), 6.9 (m, 2H, Ph-H), 7.0 (m, 2H, Ph-H), 7.6 (br, s, 2H, NH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 28.9 (CH_3, C), 44.4 (*meso*, C), 20.9 (CH_3, C), 106.1 (β′-C, pyrrole), 108.2 (β-C, pyrrole), 116.8 (α′-C, pyrrole), 136.3 (Ph-C), 144.3 (Ph-C); IR (KBr): ν 3422.5 (pyrrole NH), 3123.3 (β-pyrrole C–H), 2986.9, 2870.2, 1666.3, 1552.4, 1559.9, 1509.4, 1454.8, 1414.2, 1269.4, 1027.5, 882.8, 801.0, 777.2 and 725.5 cm^{-1}; MS(EI) *m/z*: 250.1 (M^+), 249.2 ($M^+ - 1$), 237 (M^+-CH_3), 184.1 (100%) (M^+-pyrrole).

Compound ***5***: 92%; light creamish solid, mp 277°C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.4 (m, 8H, C_6H_{10}), 1.48 (m, 16H, C_6H_{10}), 1.9 (m, 16H, C_6H_{10}), 5.89 (d, 8H, pyrrole), 7.0 (br, s, 4H, NH); IR (KBr): ν 3433.9 (pyrrole NH), 3104.48 (β-pyrrole C–H), 2985.2, 2856.7, 1702.19, 1570.9, 1447 and 1215.3 cm^{-1}; MS(EI) *m/z*: 589.5 [$M^+ + 1$].

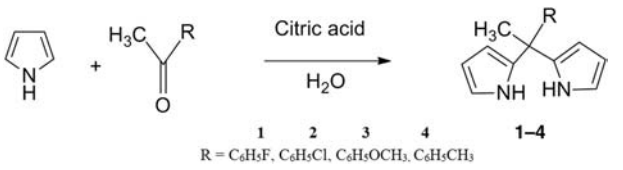
Compound ***6***: 95%; light creamish solid, mp 298°C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.5 (s, 24H, CH_3), 5.90–5.89 (m, 8H, pyrrole-H), 7.01 (br, s, 4H, NH); IR (KBr): ν 3441.8 (pyrrole NH), 3108.7 (β-pyrrole C–H), 2969.6, 2931.0, 1578.0, 1507.3, 1279.6, 775.1 and 760.1; MS(EI) *m/z*: 429.2 [$M^+ + 1$].

Compound ***7***: 82%; light creamish solid, mp 145°C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.75 (m, 12H, CH_3, CH_2CH_3), 1.45 (s, 24H, CH_3), 1.85 (m, 8H, CH_2CH_3), 5.8 (m, 8H, pyrrole-H), 7.1 (br, s, 4H, NH); IR (KBr): ν 3441.5 (pyrrole NH), 3106.5 (β-pyrrole C–H), 2969.1, 2931.0, 2870.4, 1640.1, 1578.0, 1414.0 (C–H bending), 1381.1, 964.0 and 725.1 cm^{-1}; MS(EI) *m/z*: 485.4 [$M^+ + 1$].

Compound ***8***: 40%; light creamish solid, mp 217°C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.8 (s, 12H, CH_3), 5.67–5.65 (d, 8H, pyrrole-H), 6.9–7.0 (m, 8H, phenyl-H), 7.1–7.2 (m, 12H, phenyl CH) 7.5 (br, s, 4H, NH); IR (KBr): ν 3438.4 (pyrrole NH), 3105.0 (β-pyrrole C–H), 2975.0, 2873.4, 1596.7, 1575.0, 1491.3, 1444.9 1416.2, 1215.6, 1026.1, 769.9, 700.1 and 506.2 cm^{-1}; MS(EI) *m/z*: 677.5 [$M^+ + 1$].

Results and discussion

Compounds **1–4** were prepared in good yields by refluxing pyrrole and substituted acetophenone in 2:1 ratio with weak organic acid (citric acid) as catalyst and water as solvent till completion of the reaction (Scheme 1). Weak organic acids are not only inexpensive and non-hazardous but also good catalysts; these can be easily removed by washing with water.



Scheme 1. Syntheses of 5-methyl-5-aryldipyrromethanes.

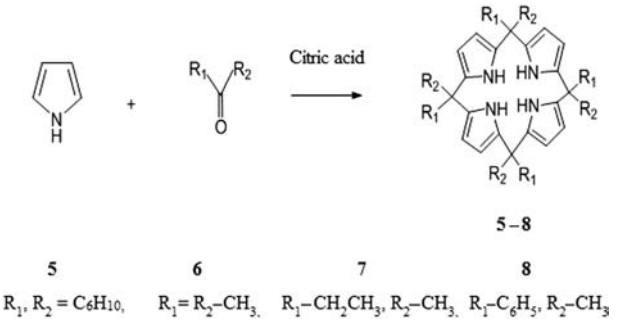
They catalyse the reaction of pyrrole with substituted acetophenone in a selective and greener way giving dipyrromethanes of high purity. Not many oligomeric and polymeric products have been detected in workup even on long exposure. Citric acid failed to catalyse the condensation reaction of pyrrole with benzophenone even on refluxing for extended periods. To extend the scope of the reaction, calix[4]pyrroles (*5–8*) have also been synthesised by condensation of pyrrole in the presence of excess of ketone as solvent (cycohexanone, acetone, methylethylketone and methyphenylketone) using the same catalyst (Scheme 2).

Crystals of **2–4** suitable for X-ray crystallographic analysis were obtained from ethanol–water mixture. All the crystal systems are monoclinic with space group $P2_1/c$ for **2** and $P2_1/n$ for **3** and **4** (Table 1). In crystal structures of **2–4**, *meso*-sp^3 C atom is slightly deviated from tetrahedral geometry as bulky aryl group leads to steric crowding around it (Figures 1–3).

The pyrrolic NH protons are involved in intermolecular H-bonding interactions with the oxygen of anisole group (Figure 2(b)) in **3**. No significant hydrogen bonding interactions have been observed in **2** and **4**.

Anion binding studies

The anion binding properties of various substituted methylaryldipyrromethanes **1–4** were investigated with different anions (F^-, Cl^-, CH_3COO^-, $H_2PO_4^-$ and HSO_4^-) by ^{1}H NMR titrations in $CDCl_3$ at room temperature.



Scheme 2. Syntheses of calix[4]pyrroles.

Table 1. Crystallographic data and structural refinement method for compounds **2**–**4**.

	2	**3**	**4**
Empirical formula	$C_{16}\ H_{15}\ Cl\ N_2$	$C_{17}\ H_{18}\ N_2\ O$	$C_{17}\ H_{18}\ N_2$
Formula weight	270.75	266.34	250.33
Crystal system	Monoclinic	Monoclinic	Monoclinic
Crystal size (mm)	$0.16 \times 0.12 \times 0.11$	$0.15 \times 0.11 \times 0.10$	$0.18 \times 0.16 \times 0.12$
Colour	Colourless	Colourless	Colourless
Shape	Needle	Square	Needle
Space group	$P2_1/c$	$P2_1/n$	$P2_1/n$
Unit cell dimensions	$a = 16.400(4)$ Å	$a = 11.1489(4)$ Å	$a = 15.281(3)$ Å
	$b = 9.397(2)$ Å	$b = 10.5641(4)$ Å	$b = 6.4384(12)$ Å
	$c = 18.233(5)$ Å	$c = 12.3010(4)$ Å	$c = 15.508(3)$ Å
	$\alpha = 90.00°$	$\alpha = 90.00°$	$\alpha = 90.00°$
	$\beta = 93.815(12)°$	$\beta = 91.169(2)°$	$\beta = 112.135(7)°$
	$\gamma = 90.00°$	$\gamma = 90.00°$	$\gamma = 90.00°$
Volume (Å^3), Z	2803.9(11), 8	1448.49(9), 4	1413.3(5), 4
ρ_{calc} (g cm^{-3})	1.283	1.221	1.176
M (cm^{-1})	0.260	0.077	0.070
$F(0\,0\,0)$	1136	568	536
Range of data collection, θ	1.24–28.59	2.44–32.48	1.59–31.35
Limiting frequency	$-20 \le h \le 21$	$-16 \le h \le 16$	$-22 \le h \le 22$
	$-12 \le k \le 11$	$-15 \le k \le 14$	$-5 \le k \le 9$
	$-24 \le l \le 24$	$-18 \le l \le 17$	$-22 \le l \le 20$
Total reflections	26,538	20,872	17,372
Independent reflections	7016	5207	4616
Completeness to θ (%)	97.8	99.5	99.3
Refinement method	Full matrix least squares on F^2	Full matrix least squares on F^2	Full matrix least squares on F^2
Goodness of fit on F^2	1.017	1.024	1.029
Final R indices [$I > 2(I)$]	$R_1 = 0.0522$, $wR_2 = 0.1263$	$R_1 = 0.0491$, $wR_2 = 0.1306$	$R_1 = 0.0506$, $wR_2 = 0.1338$
R indices (all data)	$R_1 = 0.1182$, $wR_2 = 0.1622$	$R_1 = 0.0795$, $wR_2 = 0.1496$	$R_1 = 0.0788$, $wR_2 = 0.1538$
Largest diff. peak and hole (e Å^3)	0.294 and −0.332	0.272 and −0.197	0.226 and −0.227

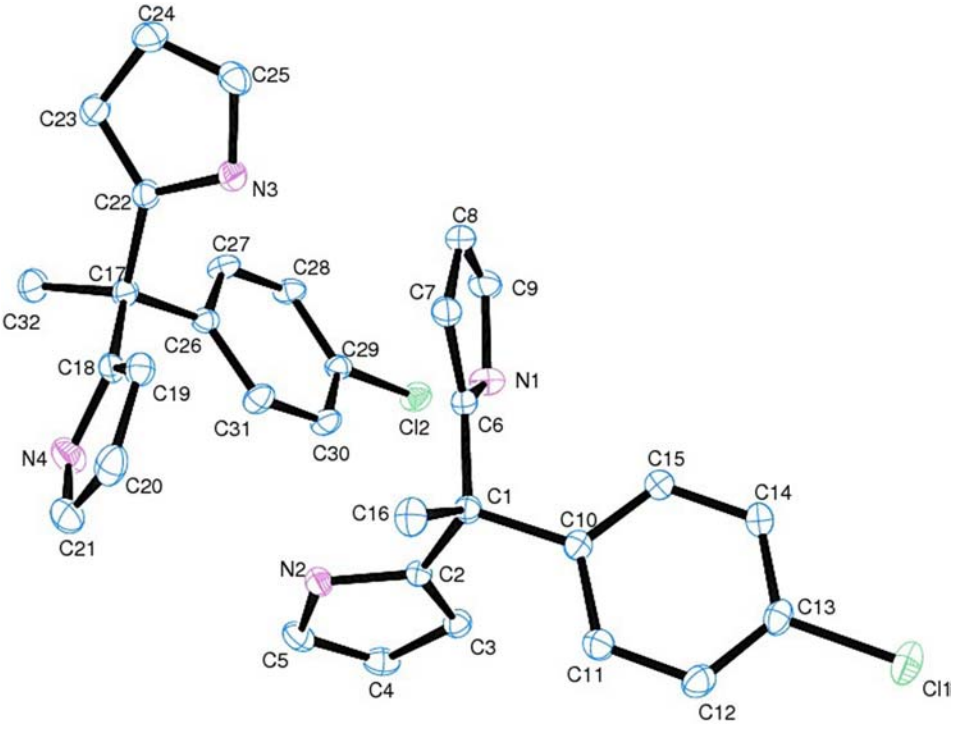


Figure 1. (colour online) ORTEP diagram of 5-methyl-5-(4-chlorophenyl)dipyrromethane **2**.

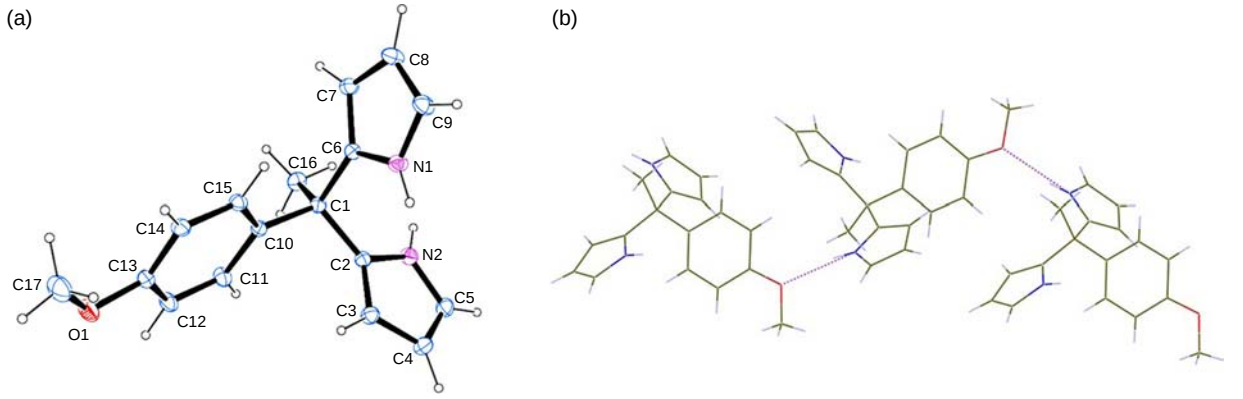


Figure 2. (colour online) (a) ORTEP diagram of 5-methyl-5-(4-methoxyphenyl)dipyrromethane **3** and (b) intermolecular H-bonding interactions showing one-dimensional array.

Stability constants were determined using the EQNMR (*13*) computer program for fitting the binding profiles to a 1:1 methylaryldipyrromethane–anion solution complex model by observing the shifts of NH protons of pyrrole. The anions were added in the form of tetrabutylammonium salts and their concentrations ranged from 0.0011 to 0.036 M while the concentration of **1**–**4** was kept constant, 0.0045 M, during the ^{1}H NMR titration experiment. The results summarised (Table 2) revealed that compounds **1**–**4** bind strongly with fluoride ion as compared with other anions with 1:1 stoichiometry. The titration profile (Figure 4) showed pronounced changes observed in the NMR spectra of **1** by the addition of fluoride ion. The signal corresponding to the pyrrolic NH protons initially

Table 2. The association constants of the complexes of **1**–**4** with anions determined by NMR titrations.[a]

	F^-	Cl^-	CH_3COO^-	$H_2PO_4^-$	HSO_4^-
1	2.23	1.65	1.78	1.84	1.44
2	2.51	2.01	2.00	1.78	1.24
3	2.26	1.85	1.64	1.39	1.78
4	2.13	1.35	1.70	1.46	1.24

Note: K values are $\log_{10}$ values.
[a] Errors are $<6.0\%$.

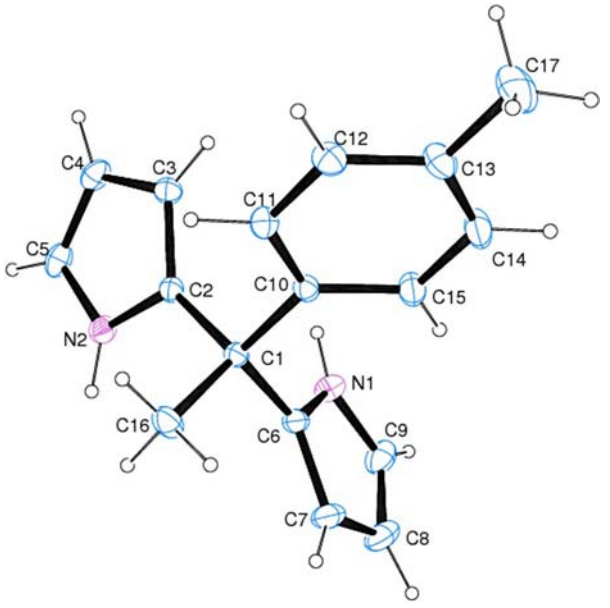


Figure 3. (colour online) ORTEP diagram of 5-methyl-5-(4-methylphenyl)-dipyrromethane **4**.

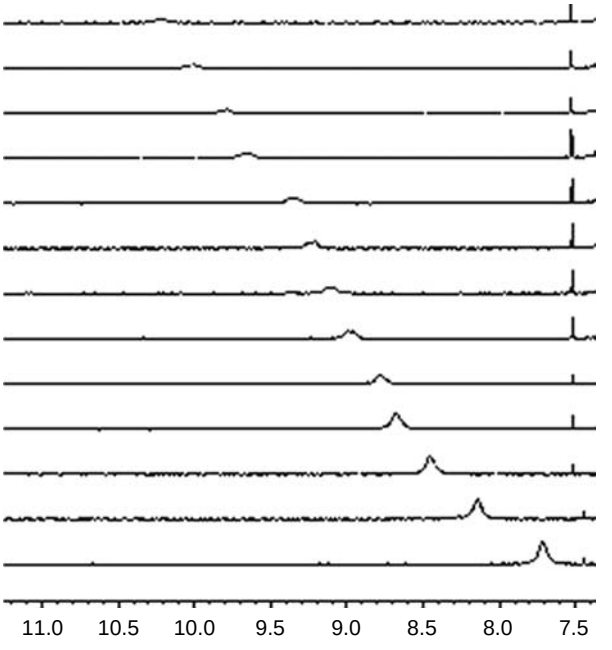


Figure 4. ^{1}H NMR spectra of **1** with varying concentration of Bu_4NF. The bottom spectrum corresponds to pure **1,** whereas other spectra correspond to **1** and the following fluoride ion concentrations: 0.25, 0.50, 0.75, 1.0, 1.25, 1.50, 1.75, 2.0, 3.0, 4.0, 6.0 and 8.0 g equiv.

appeared at 7.71 ppm was deshielded to 8.78 ppm on addition of 1.0 equiv. of fluoride ion, thus showing a downfield shift of NH signal ($\Delta\delta = 1.07$ ppm) along with the splitting of signal at 1.25 equiv. which is the hallmark of strong binding (*14*). It has been found that the signal corresponding to NH proton in compound **1** does not disappear even on addition of excess of tetrabutylammonium fluoride (S 44). No signal is observed in the range of 15.0–16.0 ppm corresponding to $[FHF]^-$, indicating that deprotonation is not taking place (S 45). However, the decrease in peak height corresponding to NH protons can be attributed to H-bonding interactions. On addition of 1.0 equiv. of anion, α-CH proton of pyrrole near the binding site experienced downfield shift from 6.62 to 6.71 ppm. At the same time, two β-CH protons and phenyl CH protons underwent a reasonable downfield shift (0.03 and 0.09 ppm for pyrrolic CH; 0.02 and 0.07 ppm for phenyl CH) (Supplementary data, available online). These shifts showed that anion has induced electronic perturbations in the receptor or host molecule.

Chloride, acetate, dihydrogen phosphate and hydrogen sulphate ions have also induced downfield shift of NH protons ($\Delta\delta = 0.21$, 0.6637, 0.835 and 0.0685) in the same receptor **1** due to their larger size, smaller basicity and lesser nucleophilicity but to a smaller extent than fluoride ion. Addition of 1 equiv. of fluoride ion to **2, 3** and **4** showed a downfield shift of NH signal $\Delta\delta = 1.43$, 0.88, 0.64 ppm, respectively. The addition of other anions (Cl^-, CH_3COO^-, $H_2PO_4^-$ and HSO_4^-) to the solutions of **2**–**4** also showed downfield shift of NH signal.

Compounds **1**–**4** are most selective towards fluoride as compared with other anions and least selective towards hydrogen sulphate ion with the exception of **3** having methoxyphenyl group at *meso*-position. The latter is least sensitive towards dihydrogen phosphate ion. The results obtained from anion binding studies showed that the compounds (Table 2) substituted with electron-withdrawing group (**1**, **2**) have higher binding constants than compounds with electron-releasing group (**3**, **4**). Compound **2** with chlorophenyl substituent at *meso*-position shows higher value of binding constant as than **1** with fluorophenyl substituent at *meso*-position that may be attributed to the presence of intermolecular hydrogen bonding interactions between NH protons of one molecule and the fluoro group present at the phenyl ring of another molecule in **1**. Similar interactions have also been reported in the literature in case of β-monofluorocalix[4]pyrrole that bound bromide, dihydrogen phosphate, hydrogen sulphate less strongly than β-monochlorocalix[4]pyrrole (*15*).

Conclusion

In summary, we have reported the synthesis of 5-methyl-5-aryldipyrromethanes **1**–**4** and calix[4]pyrroles **4**–**8** in the presence of milder, eco-friendly and versatile catalyst that catalyses the reactions in a selective and greener way, giving products of high purity. 5-Methyl-5-aryldipyrromethanes **1**–**4** have been proved to be anion sensors using ^{1}H NMR spectroscopic analysis. It has been observed that introduction of electron-withdrawing groups enhanced the binding ability of receptors as compared with electron-releasing groups. All these receptors have more affinity towards F^- ion than towards other anions as is evident from their association constants (Table 2), yielding 1:1 complexes. The binding constants calculated for compounds **1**–**4** with fluoride ion (reported in the present work) are higher than those for 1:1 complex of fluoride with diphenyldipyrromethane (*4a*). This may be attributed to less steric crowding in methylaryldipyrromethane compared with diphenyldipyrromethane at the *meso*-position. Anion sensors with low value of binding constant can be used as HPLC media for the separation of mixture of compounds.

Supplementary data

Supplementary data contain experimental procedures, ^{1}H NMR, mass spectra **1**–**8** and ^{13}C NMR and binding profiles for compounds **1**–**4**. Crystal data for **2**–**4** are presented in CIF format. Crystallographic data (excluding structure factors) for the structure in this paper have been deposited with the Cambridge Crystallographic Data Centre, as supplementary publication number, CCDC Nos 923726, 898492 and 916187. Copies of data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-(0) 1223-336033 or email: deposit@ccdc.cam.ac.uk).

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