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Dae-Wi Yoon[a]; Seong-Doo Jeong[a]; Mee-Young Song[a]; Chang-Hee Lee[a]
[a] Department of Chemistry, Kangwon National University, Chun-Cheon, South Korea

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Calix[6]pyrroles Capped with 1,3,5-Trisubstituted Benzene

DAE-WI YOON, SEONG-DOO JEONG, MEE-YOUNG SONG and CHANG-HEE LEE*

Department of Chemistry, Kangwon National University, Chun-Cheon 200-701, South Korea

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One side of the calix[6]pyrrole, capped with 1,3,5-trisubstituted benzene, have been synthesized for the first time and fully characterized. The synthesis of the target systems were accomplished by acid-catalyzed cyclization of ester/ether-functionalized tripodal dipyrromethanes. The solution state binding studies of the capped calix[6]pyrroles revealed a slow complexation/decomplexation kinetics for fluoride anion and chloride anion. The results indicated that fluoride anion binds inside the cavity with 1/1 binding stoichiometry. On the other hand, only four pyrrolic N-Hs participate in chloride anion binding.

Keywords: Calix[6]pyrrole; Capped-calix[6]pyrroles; Anion binding; Expanded calixpyrroles

INTRODUCTION

Anions play many important roles in biological systems and synthesis of neutral anion receptors possessing higher specificity [1–3] has been an ongoing challenge in supramolecular anion-binding chemistry. Among the various neutral anion receptors reported to date, *meso*-octamethylporphyrinogen so-called 'calix[4]pyrrole' have been well documented since 1996 as readily accessible neutral anion receptors. Various functionalizations and modifications of the mother macrocycles have been documented in conjunction with improving recognition properties [4–10]. More recently several new systems bearing a diametrical strap on one side of the calix[4]pyrrole have been introduced and demonstrated superior affinity and selectivity for halide anions including carboxylate anions [11,12]. These findings inspired us to pursue further complex design and modification of the mother macrocycle for higher selectivity and affinity to various anions other than halide anions. One feasible approach for these purposes will be expanding the binding domain of the calix[4]pyrrole. Calix[n]pyrroles ($n = 6,8$) would be good models for non-spherical anions due to possible existence of the 3-D binding domain. Calix[6]pyrroles have been synthesized and studied for complexation with halide anions and bulk-membrane transport of anions [13]. Calix[6]pyrroles have been reported to form stable 1/1 complex with a chloride or bromide anion. These stable complex formations have been attributed to the larger cavity size [14,15]. The hybrid calix[6]pyrroles and extended cavity calix[6]pyrroles also have been synthesized [16,17] and found to form strong complex with iodide anion. Since expanded calixpyrroles can recognize larger anions, further confinement of the binding domain of calix[6]pyrroles may exhibit increased selectivity and affinity especially for non-spherical anions. With these regards, we here report the convenient syntheses of capped calix[6]pyrroles and their solution state binding chemistry with halide anions.

RESULTS AND DISCUSSION

The key part in the design of capped calix[6]pyrrole is the synthesis of precursor which can afford the desired product in a single step. This can be achieved by the introduction of three flexible straps on trisubstituted benzene. As shown in Scheme 1, the synthesis is accomplished in four steps starting from 1,3,5-trihydroxybenzene.

6-Bromo-2-hexanone (**1**) or 7-bromo-2-heptanone (**2**) were reacted with pyrrole in the presence of acid to afford corresponding dipyrromethanes (**3**) and (**4**), which were successively reacted with 1,3,5-trihydroxybenzene to give tripodal-dipyrromethane

*Corresponding author. E-mail: chhlee@kangwon.ac.kr

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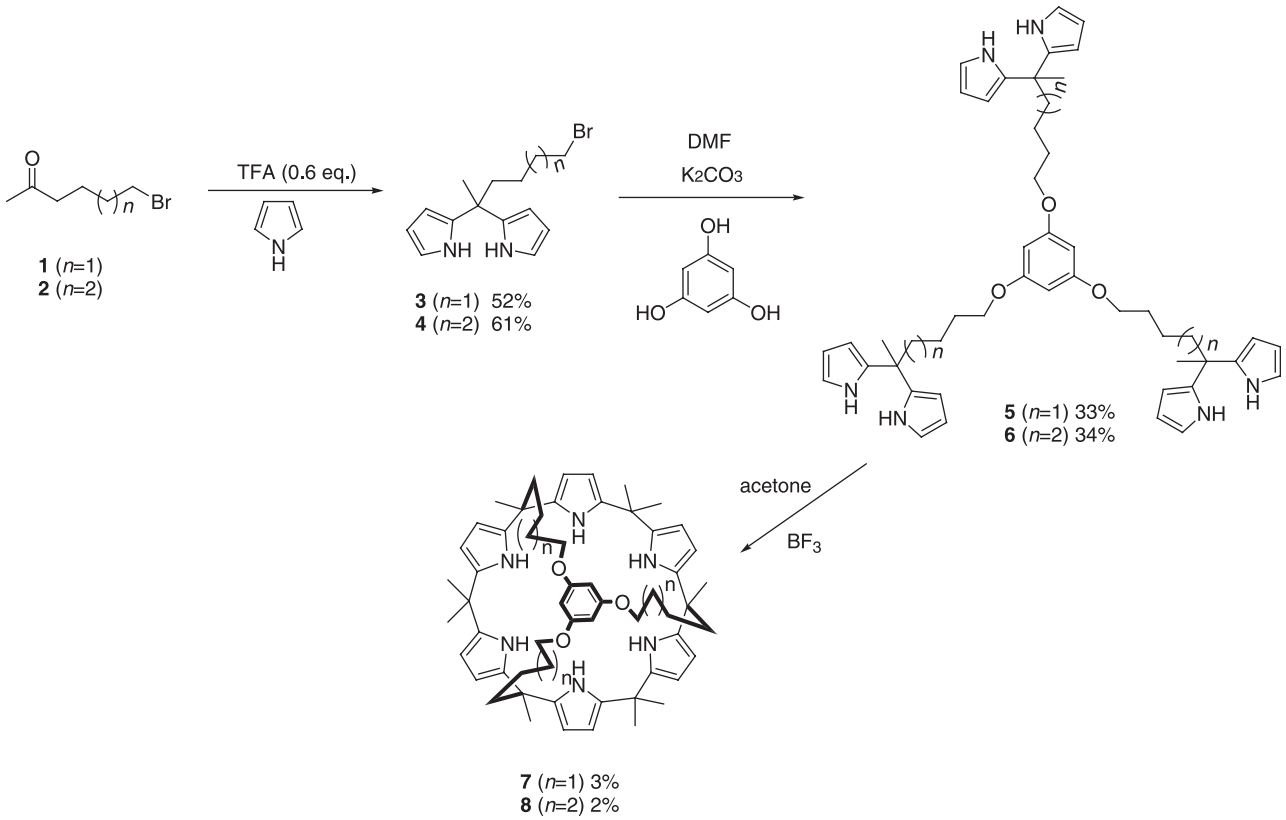


SCHEME 1

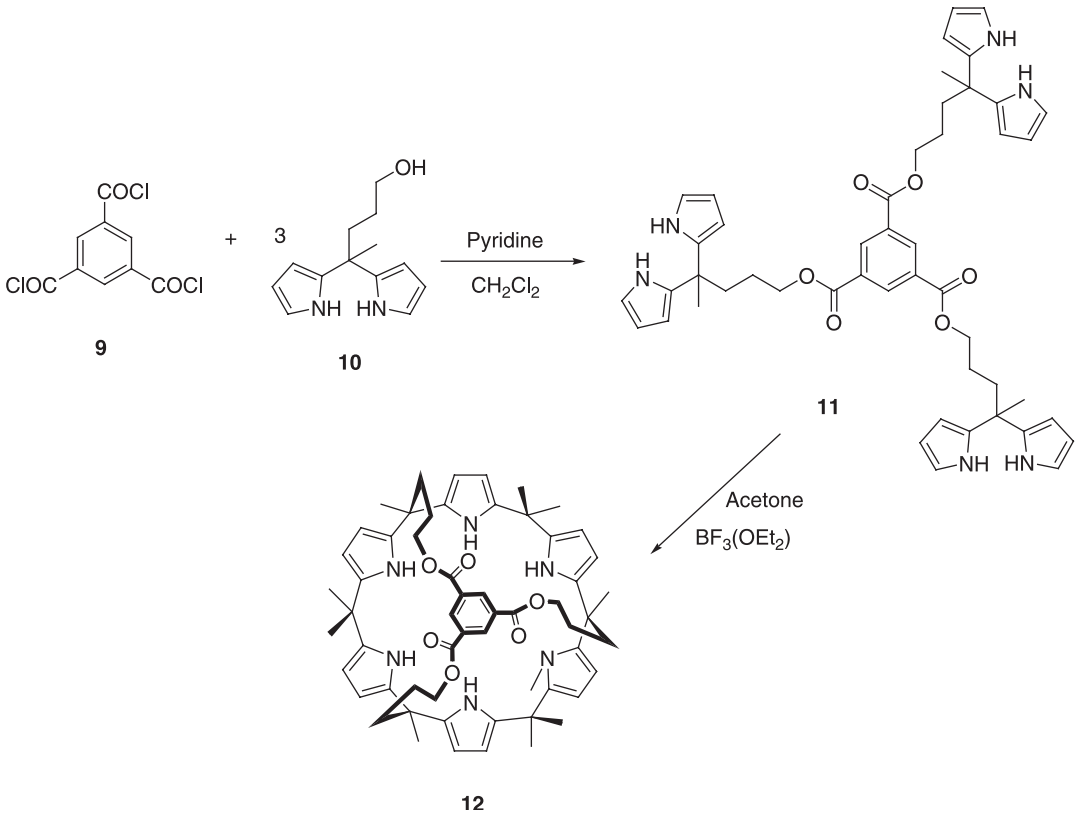
(**5**) and (**6**). Acid-catalyzed condensation of (**5**) or (**6**) with acetone resulted in the formation of desired capped calix[6]pyrroles (**7**) and (**8**) in low yields. This intramolecular condensation is expected to be unfavorable and give many side products due to unfavorable geometry and transition state entropy factors. Proton NMR spectra (**7**) and (**8**) have several distinctive features. For example, the resonance of the pyrrolic NH in (**7**) appeared at 7.83 ppm as a broad singlet, while those of (**8**) appeared at 7.71 ppm. The signals of β-pyrrolic protons were shown at 5.66 ppm and 5.96 ppm, while those of (**8**) were 5.68 ppm and 5.83 ppm. The signal appeared at 2.90 ppm with well resolved integration was rather unusual and observed only in (**7**). No signal was observed in the case of (**8**). Analysis of MALDI-TOF mass spectrum of (**7**) revealed that the compound (**7**) holds one methanol molecule in the cavity tightly ($M^+ + 32 = 921.22$). Four carbon spaces between calix[6]pyrrole ring and benzene seems to be a suitable distance for methanol binding.

Capped-calix[6]pyrrole (**12**) bearing ester function on the cap part has also synthesized as shown in Scheme 2. Benzene tricarbonyl chloride (**9**) was reacted with three molar equivalence of dipyrromethane (**10**) to afford tris-dipyrromethane (**11**) in 61% yield. Compound (**11**) then condensed with acetone in the presence of BF_3 to give receptor (**12**) in 3% yield.

Preliminary anion binding properties of systems (**8**) carried out in DMSO-d_6 using proton NMR spectroscopy indicated strong affinity with fluoride anion and slow complexation/decomplexation kinetics and thus quantitative anion affinities could not be made by proton NMR spectroscopy. However, the studies provided a good qualitative evidence for halide anion binding. For example, titration of receptor (**8**) with fluoride anion studied in the form of its tetrabutylammonium salt gave rise to a new set of signals by adding just one equivalent of fluoride anion indicating 1/1 binding stoichiometry (Fig. 1).

The typical changes of the signals include the following: i) the pyrrole N—H protons appeared originally at 9.66 ppm in the absence of fluoride anion was shifted to 10.69 ppm in the presence of fluoride anion. The β-pyrrolic protons, originally appearing at 5.51 ppm and 5.32 ppm, were found to be shifted to 5.43 ppm and 5.41 ppm, respectively. The two separated β-pyrrolic signals seem to merge with each other upon binding with an anion. This observation indicates that the molecule became more symmetric upon binding with the fluoride anion.

On the other hand, titration of receptor (**8**) with a chloride anion studied in the form of its tetrabutylammonium salt showed co-existence of bound and unbound pyrrole N-Hs (Figure 2). The ratio between bound and unbound pyrrole N-Hs converges to 4/2 even in the presence of excess chloride



SCHEME 2

anion (over 12 equivalents). Careful analysis of the integration and shifts in resonance lines in the ^1H NMR spectra revealed that only four pyrrole N-Hs participate in binding with the chloride anion and the other two pyrrole N-Hs remained unbound even in higher chloride concentration. These results indicate that the current systems are rather sensitive to the size of the anion and the chloride anion is rather too large to fit inside the binding cavity. Once the chloride anion occupies the cavity, the host molecule may be conformationally locked and lose most of its conformational degree of freedom. Accounting for all these observations, including the up-field shift of aryl-H, unusual conformational changes must be involved with chloride anion binding. Although the exact conformational nature of the calix[6]pyrrole moiety is not known at this point, it must be quite symmetric in nature.

CONCLUSIONS

We have demonstrated that the capped calix[6] pyrroles could be successfully synthesized. The system did show appreciable selectivity for fluoride anion in organic solvent. Proper encapsulation of binding sites show that well defined binding domains with customized anion receptors is possible. Work along these lines is currently in progress.

EXPERIMENTAL

Proton NMR spectra (400 MHz, Bruker DPX-400) were recorded using TMS as the internal standard. High and low resolution FAB mass spectra were obtained on an AUTO SPEC M-363 high-resolution mass spectrometer. Column chromatography was performed over silica gel (Merck, 230–400 mesh). Pyrrole was distilled at atmospheric pressure from CaH_2. All other reagents were obtained from Aldrich and used as received unless noted otherwise.

5-(4-Bromobutyl)-5-methyldipyrromethane (3)

6-Bromo-2-hexanone (4.0 g, 22.34 mmol) was dissolved in neat pyrrole (31 mL, 446.80 mmol) with stirring and trifluoroacetic acid (1.03 mL, 13.40 mmol) was added. The mixture was stirred for 2 hr at room temperature. Then the reaction was quenched by adding aqueous NaOH (0.1 N, 50 mL) and extracted with CH_2Cl_2 (30 mL × 3). The organic layer was dried (Na_2SO_4) and the solvent was removed *in vacuo*. The resulting solid was purified by column chromatography on silica gel (CH_2Cl_2). Yield: 3.5 g (52%); ^1H NMR ($CDCl_3$) δ 1.30–1.38 (m, 2H, CH_2), 1.59 (s, 3H, CH_3), 1.78–1.85 (m, 2H, CH_2), 1.95–2.00 (m, 2H, CH_2), 3.36 (t, 2H, $J = 7.0$ Hz, CH_2), 5.96 (br s, 2H, pyrrole-H), 6.13–6.14 (m, 2H, pyrrole-H), 6.62 (m, 2H, pyrrole-H), 7.72 (s, 2H, NH);

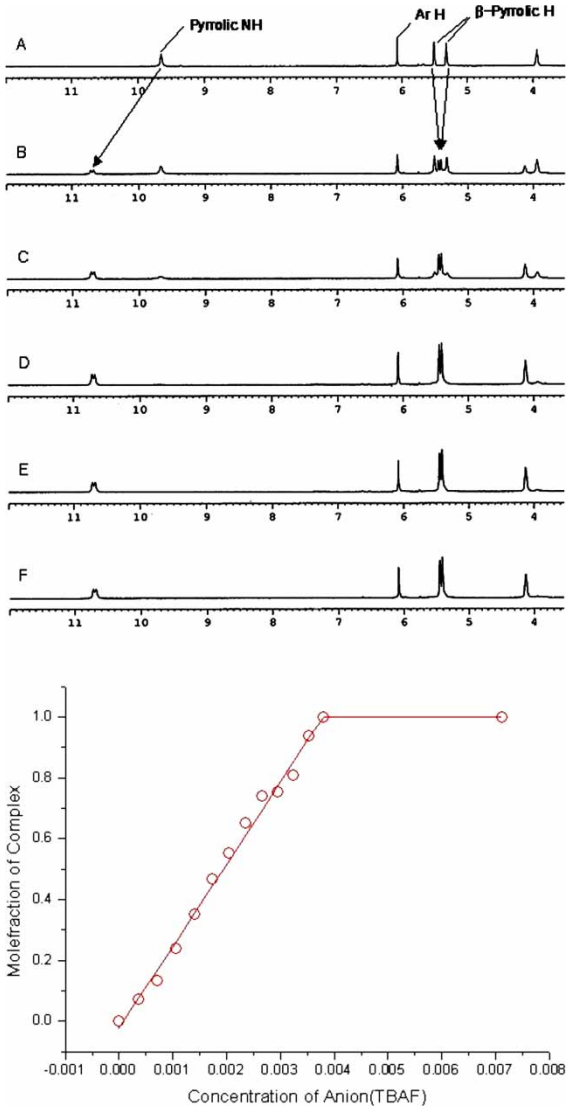


FIGURE 1 Titration of (**8**) with fluoride anion (as its tetrabutylammonium salt) in DMSO-d_6. ([**8**] = 4.08 mM). A) free host, B) 0.36 C) 0.64 D) 0.99 E) 1.09 F) 2.34 equiv. respectively. The bottom graph is the titration curve showing that 1/1 binding stoichiometry with slow equilibrium at 25°C.

^{13}C NMR ($CDCl_3$) δ 23.63, 26.65, 33.52, 33.97, 39.40, 40.77, 105.00, 108.20, 117.47, 138.15; FAB MS Calcd. for $C_{14}H_{19}BrN_2$ 294.07, Found 294.07.

5-(5-Bromopentyl)-5-methyldipyrromethane (4)

7-Bromo-2-heptanone (5.8 g, 30.08 mmol), pyrrole (42 mL, 601.6 mmol) and trifluoroacetic acid (1.39 mL, 18.05 mmol) were treated identically as for the synthesis of (**3**). Yield: 5.67 g (61%); ^{1}H NMR ($CDCl_3$) δ 1.17–1.28 (m, 2H, CH_2), 1.36–1.44 (m, 2H, CH_2), 1.57 (s, 3H, CH_3), 1.78–1.85 (m, 2H, CH_2), 1.93–1.98 (m, 2H, CH_2), 3.35 (t, 2H, J = 6.8 Hz, CH_2), 6.06–6.08 (m, 2H, pyrrole-H), 6.12–6.14 (m, 2H, pyrrole-H), 6.61–6.62 (m, 2H, pyrrole-H), 7.70 (s, 2H, NH); ^{13}C NMR ($CDCl_3$) δ 24.06, 26.65, 29.05, 33.10, 34.33, 39.40, 41.44, 104.98, 108.09, 117.45, 138.41; FAB MS Calcd. for $C_{15}H_{21}BrN_2$ 308.09, Found 309.00 (MH^+).

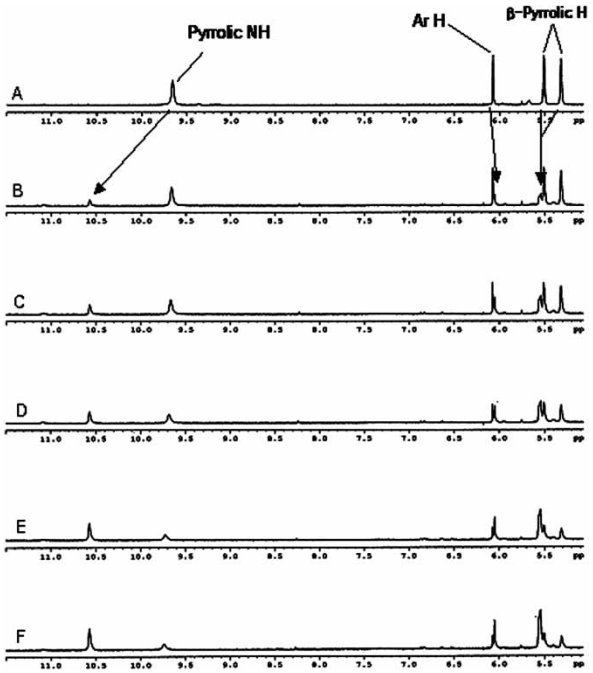


FIGURE 2 Titration of (**8**) with chloride anion (as its tetrabutylammonium salt) in DMSO-d_6. ([**8**] = 2.58 mM). A) free host; B) 0.47; C) 0.94; D) 1.91; E) 5.87; F) 12.11 equiv. respectively.

1,3,5-Tris[5,5-di-(1*H*-pyrrol-2-yl)hexyloxy] benzene (5)

5-(4-Bromobutyl)-5-methyldipyrromethane (**3**) (0.27 g, 0.92 mmol) and K_2CO_3 (0.85 g, 6.12 mmol) were mixed in DMF (11 mL) and the mixture was stirred for 10 min. Then, 1,3,5-trihydroxybenezene (0.05 g, 0.31 mmol) was added and the whole mixture was stirred for 24 hr at 60°C. The mixture was cooled to room temperature and combined with water (20 mL) and extracted with CH_2Cl_2 (50 mL × 3). The organic layer was dried (Na_2SO_4) and the solvent was removed *in vacuo*. The resulting solid was purified by column chromatography on silica gel (CH_2Cl_2/EtOAc = 19/1). Yield: 0.08 g (33%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.23–1.33 (m, 6H, CH_2), 1.54 (s, 9H, CH_3), 1.66–1.72 (m, 6H, CH_2), 2.00–1.94 (m, 6H, CH_2), 3.80–3.83 (m, 6H, CH_2), 5.98 (s, 3H, Ar-H), 6.05–6.07 (m, 6H, pyrrole-H), 6.09–6.11 (m, 6H, pyrrole-H), 6.51–6.52 (m, 6H, pyrrole-H), 7.54 (s, 6H, NH); ^{13}C NMR ($CDCl_3$) δ21.46, 26.73, 29.95, 39.40, 41.21, 68.19, 94.33, 105.10, 108.04, 117.53, 138.45, 161.23; FAB MS Calcd. for $C_{48}H_{60}N_6O_3$ 768.47, Found 769.47 (MH^+).

1,3,5-Tris[6,6-di-(1*H*-pyrrol-2-yl)heptyloxy] benzene (6)

5-(5-Bromopentyl)-5-methyldipyrromethane (**4**) (1.73 g, 5.59 mmol), K_2CO_3 (3.86 g, 27.95 mmol),

DMF (69 mL) and 1,3,5-trihydroxybenezene (0.3 g, 0.31 mmol) were treated identically as for the synthesis of (**5**). Yield: 0.52 g (34%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.17–1.27 (m, 6H, CH_2), 1.35–1.42 (m, 6H, CH_2), 1.53 (s, 9H, CH_3), 1.65–1.72 (m, 6H, CH_2), 1.91–1.95 (m, 6H, CH_2), 3.81–3.84 (m, 6H, CH_2), 6.00 (s, 3H, Ar-H), 6.05–6.06 (m, 6H, pyrrole-H), 6.10–6.12 (m, 6H, pyrrole-H), 6.515–6.524 (m, 6H, pyrrole-H), 7.54 (s, 6H, NH); ^{13}C NMR ($CDCl_3$) δ 24.14, 26.24, 26.51, 29.10, 38.94, 41.04, 67.86, 93.79, 104.55, 107.59, 117.01, 138.12, 160.85; FAB MS Calcd. for $C_{51}H_{66}N_6O_3$ 810.52, Found 811.00.

Capped Calix[6]pyrrole (7)

1,3,5-Tris[5,5-di-(1*H*-pyrrol-2-yl)hexyloxy]benzene (**6**) (0.98 g, 1.28 mmol) was dissolved in acetone (200 mL) and $BF_3(OEt_2)$ (0.033 mL, 0.26 mmol) was added. The mixture was stirred for 2 hr in the dark. The mixture was combined with water (200 mL) and extracted with CH_2Cl_2 (100 mL × 3). The organic layer was dried (Na_2SO_4) and the solvent was removed. The resulting solid was purified by column chromatography on silica gel (CH_2Cl_2). The pure product was obtained by recrystallization from CH_2Cl_2/methanol. Yield: 0.03 g (3%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.30–1.36 (m, 6H, CH_2), 1.45 (s, 9H, CH_3), 1.50 (s, 9H, CH_3), 1.58 (s, 9H, CH_3), 1.76–1.77 (m, 6H, CH_2), 1.85–1.89 (m, 6H, CH_2), 3.93 (br s, 6H, CH_2), 5.66 (br s, 6H, pyrrole-H), 5.96 (s, 9H, Ar-H, pyrrole-H), 7.83 (s, 6H, NH); ^{13}C NMR ($CDCl_3$) δ 23.35, 28.66, 28.88, 29.70, 30.23, 35.78, 40.02, 43.20, 67.82, 92.95, 103.91, 104.09, 136.86, 138.23, 160.95; MALDI-TOF MS Calcd. for $C_{57}H_{72}N_6O_3$ 889.22, Found 889.71.

Capped Calix[6]pyrrole (8)

1,3,5-Tris[5,5-di-(1*H*-pyrrol-2-yl)hexyloxy]benzene (**6**) (0.53 g, 0.65 mmol), acetone (170 mL), $BF_3(OEt_2)$ (0.017 mL, 0.13 mmol) were treated identically as for the synthesis of (**7**). Yield: 0.013 g (2%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.19 (br s, 6H, CH_2), 1.33 (s, 9H, CH_3), 1.50 (s, 9H, CH_3), 1.56 (s, 9H, CH_3), 1.66–1.71 (m, 6H, CH_2), 1.83–1.87 (m, 6H, CH_2), 4.01 (t, 6H, $J = 6.3$ Hz, CH_2), 5.68 (br s, 6H, pyrrole-H), 5.83 (br s, 6H, pyrrole-H), 6.08 (s, Ar-H), 7.71 (s, 6H, NH); ^{13}C NMR ($CDCl_3$) δ 24.48, 25.05, 27.71, 29.51, 29.89, 30.53, 35.78, 39.94, 42.72, 66.77, 95.18, 103.82, 104.06, 136.66, 138.02, 160.22; FAB MS Calcd. for $C_{60}H_{78}N_6O_3$ 930.61, Found 931.67 (MH^+).

5-(3-Hydroxypropyl)-5-methyldipyrromethane (10)

4-Oxo-1-pentanol (2 mL, 19.7 mmol) was dissolved in pyrrole (10 mL, 137.9 mmol) and trifluoroacetic acid (0.2 mL, 2.56 mmol) was added. The mixture was stirred for 5 min at room temperature. The reaction was quenched immediately by adding aqueous NaOH (0.1 N, 20 mL) and extracted with CH_2Cl_2 (30 mL × 3). The organic layer was dried (Na_2SO_4) and the solvent was removed. The resulting solid was purified by column chromatography on silica gel (CH_2Cl_2/EtOAc = 1/1). The pure product was obtained by recrystallization from EtOAc/CH_2Cl_2. Yield: 3.34 g (78%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.44–1.51 (m, 2H, CH_2), 1.60 (s, 3H, CH_3), 2.03–2.07 (m, 2H, CH_2), 3.58–3.60 (m, 2H, CH_2), 6.08–6.10 (m, 2H, pyrrole-H), 6.12–6.14 (m, 2H, pyrrole-H), 6.62–6.64 (m, 2H, pyrrole-H), 7.84 (s, 2H, NH).

Benzene-1,3,5-tricarboxylic acid Tris[4,4-bis (1*H*-pyrrol-2-yl)-pentyl]ester (11)

5-(3-hydroxypropyl)-5-methyldipyrromethane (**10**) (2.76 g, 12.64 mmol) and pyridine (1.28 mL, 15.8 mmol) were dissolved in CH_2Cl_2 (316 mL) and 1,3,5-benzenetricarbonyltrichloride (0.84 g, 3.16 mmol) was added. The mixture was stirred for 24 h at room temperature. The mixture was combined with water (200 mL) and extracted with CH_2Cl_2 (100 mL × 3). The organic layer was dried (Na_2SO_4) and the solvent was removed. The resulting solid was purified by column chromatography on silica gel (CH_2Cl_2/EtOAc = 9/1). The precipitated solid after removal of the solvent was also desired product. Yield: 1.57 g (61%); ^{1}H NMR (400 MHz, THF-d_8) δ 1.56 (s, 9H, CH_3), 1.64–1.71 (m, 6H, CH_2), 2.09–2.13 (m, 6H, CH_2), 4.27 (t, 6H, $J = 6.7$ Hz, CH_2), 5.95 (m, 12H, pyrrole-H), 6.56–6.57 (m, 6H, pyrrole-H), 8.78 (s, 3H, Ar-H), 9.45 (s, 6H, NH); ^{13}C NMR (THF-d_8) δ 25.38, 27.34, 38.56, 39.98, 67.00, 105.34, 107.69, 117.70, 132.78, 134.81, 138.69, 165.36; FAB MS Calcd. for $C_{48}H_{54}N_6O_6$ 810.41, Found 811.00.

Capped Calix[6]pyrrole (12)

Benzene-1,3,5-tricarboxylic acid tris[4,4-bis(1*H*- pyrrol-2-yl)pentyl]ester (**11**) (1.28 g, 1.58 mmol) was dissolved in small amount of THF and then acetone (158 mL) was added. $BF_3(OEt_2)$ (0.041 mL, 0.32 mmol) was added to the reaction mixture and stirred for 1 h at room temperature. The reaction was quenched by adding triethylamine (0.045 mL) and the solvent was removed. The resulting solid was purified by column chromatography on silica gel (EtOAc/hexanes = 1/3) to afford pure product. Yield: 23 mg (2%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.46 (s, 9H, CH_3), 1.52 (s, 9H, CH_3), 1.55 (s, 9H, CH_3), 1.72–1.71 (m, 6H, CH_2), 2.45–2.04 (m, 6H, CH_2), 4.34 (t, 6H, J = 6.4 Hz, OCH2), 5.93–5.91 (m, 6H, pyrrole-H), 5.98–5.95 (m, 6H, pyrrole-H), 7.17 (br s, 6H, NH), 8.93 (s, 3H, Ar-H); CI MS Calcd. for $C_{57}H_{66}N_6O_6$ 930.50, Found 931.68 (MH^+).

Acknowledgements

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