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ORIGINAL ARTICLE

Synthesis, crystal structure and configuration of acetylated aryl Pyrogallol[4]arenes

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Abstract A series of aryl and ferrocenyl pyrogallol[4]arenes have been synthesized by the HCl-catalyzed condensation reactions of pyrogallol with aromatic aldehydes and ferrocenecarbaldehyde. The fully acetyl and ethoxycarbonylmethoxy derivatives were also prepared and fully characterized. The crystal structures show that acylated phenyl pyrogallol[4]arene exists in *rctt* (*cis-trans-trans*) configuration, while the corresponding ferrocenyl pyrogallol[4]arene in *rccc* (all *cis*) configuration.

Keywords Calixarene · Pyrogallolarene · Pyrogallol · Ferrocenecarbaldehyde · Crystal structure · Configuration

Introduction

Calixarenes take a particular place in the study of supramolecular chemistry [1, 2]. These compounds can be modified in various ways at the phenolic hydroxy groups as well as by electrophilic substitution in the phenolic ring. Because of this, they are useful platforms for construction of novel molecular receptors for ions and neutral compounds and assembly to supramolecular architectures [3–5]. Pyrogallol[4]arene [6], also be called as hydroxyresorc[4]arene, [2] is a subgroup of calixarene and can be easily generated similarly to resorcinarene in fairly high yields by acid-condensation of pyrogallol with aldehydes [7]. The first synthesis of pyrogallol[4]arene was reported in 1999 [8]. From then on, a series of pyrogallol[4]arenes have been synthesized with emphasis of using aliphatic aldehydes to give alkyl pyrogallol[4]arenas [9–15]. However, the study of aryl pyrogallol[4]arenes derived from the reaction of aromatic aldehydes has attracted very little attention [16]. Iwanek [17] developed a template Lewis acid-catalyzed synthesis of methylene bridged methoxypyrogallol[4]arene in crown conformer from 1,2,3-trimethoxybenzene with trioxane. Recently a larger cyclic ethyl pyrogallol[6]arene is also prepared as minor product in the acid condensation of pyrogallol with proponaldehyde [18]. Because of their favorable cyclic shape, high polarity and twelve hydroxyl groups, pyrogallol[4]arenes have been used in a widely research fields such as starting material for carcerand synthesis [18, 19], liquid-crystal material [14] and complexation studies [10]. Recently self-assembly based on pyrogallol[4]arenes into large non-covalent nano-capsules, molecular vesicle, and other supramolecular architectures in both solution and in the solid state has been the focus of a number studies made by Atwood's [20], Rebek's [21], Cohen's [22] and Mattay's [23] research groups. Generally pyrogallol[4]arenes assembly is stabilized by a large number of hydrogen bonds per calixarene due to the twelve hydroxyl groups. Guests such as solvent molecules, hydrocarbons, quaternary ammonium ions, cobaltocenium and other organometallic molecules [24] can be encapsulated in the larger cavity. Our recent interests are focused on the structural modification of calixarenes for synthesis of dendritic molecules and design of new supramolecular systems. Pyrogallol[4]arenes seem to be one of the ideal candidates that are taken as a polyfunctional core for dentritic synthesis and as building platforms for supramolecular receptors. In this paper we want to report the synthesis, configuration and crystal structures of the new aryl and ferrocenyl pyrogallol[4]arenes.

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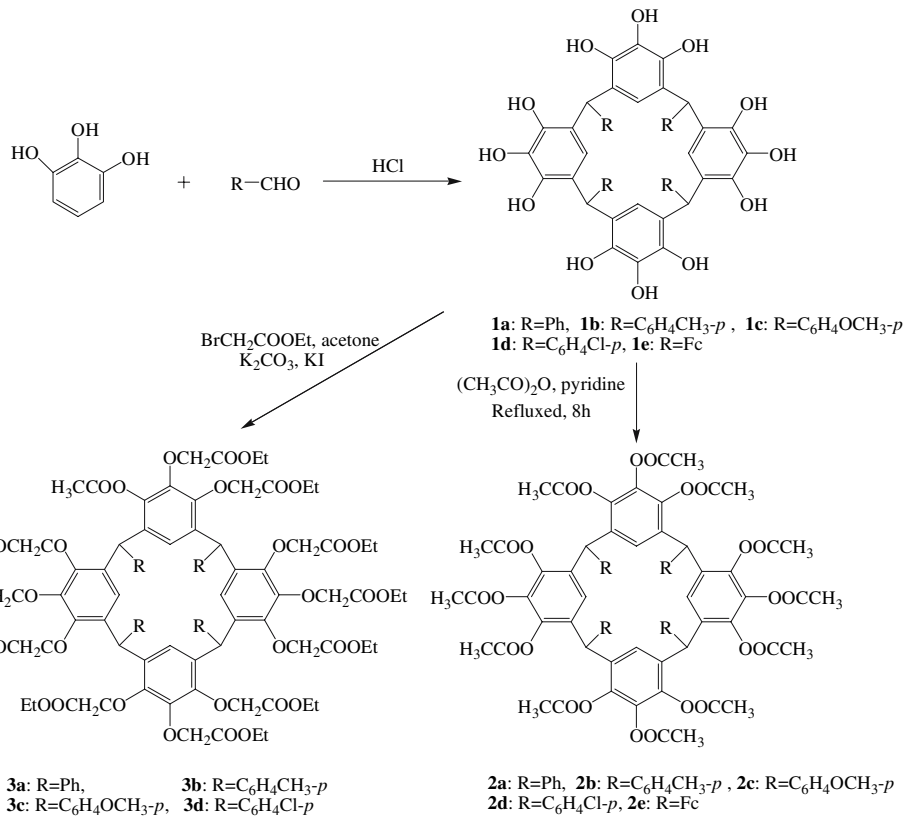
Results and discussion

The aryl pyrogallol[4]arenes **1a–1d** were synthesized by acid catalyzed cyclocondensation according to the well known procedures [8, 15] (**Scheme** 1). Thus, the concentrated hydrochloric acid was added to the solution of pyrogallol and aromatic aldehydes in 95% alcohol. Then the mixture was refluxed at 70–80 °C for 6 h. The resulted precipitate was collected by filtration to give the pink solid as aryl pyrogallol[4]arenes **1a–1d** in 63–84% yields. The ferrocenyl pyrogallol[4]arene **1e** (89%) was prepared as a dark red solid with the similar procedure by the cyclocondensation reaction of pyrogallol with ferrocenecarbaldehyde. The ferrocenyl resorcinarene has been obtained in high yield from the acid-catalyzed condensation method [25]. **1a–1e** have high melting point, do not melt at lower than 300 °C, and have very bad solubility in most organic solvents, which make great difficulty to get good characterization data for them.

In order to confirm the structure of synthetic aryl pyrogallol[4]arenes, chemical modifications with acylation and alkylation were performed. Acylation of **1a–1e** with acetic anhydride in the presence of pyridine affords the completely acylated derivatives **2a–2e** in higher yield. Because of having twelve acetate groups, **2a–2e** have very good solubility in common organic solvent and it is very convenient to get their characterization data. In their IR spectra, the acetyl C=O groups show a very strong absorption band at 1780 cm^{-1} with the disappearance of OH absorption at 3200–3500 cm^{-1} in **1a–1e**, which indicates that all hydroxyl groups in **1a–1e** have been transformed into ester groups. The ^1H NMR spectra in $CDCl_3$ usually show two singlets for protons of pyrogallol rings and methine bridges at 6.28 ppm, 5.98 ppm for **2a** and at 6.31 ppm, 5.08 ppm for **2f** for examples. The acyl groups give stronger mixed peaks at 1.90–2.20 ppm.

The *O*-alkylation of phenolic hydroxyl groups is the first choice for the modification of resorcinarenes and should be also suitable for preparating functional derivatives of pyrogallol[4]arene [26]. Aryl pyrogallol[4]arene has much lower solubility in common organic solvents, which causes some difficulty in basic alkylation reactions. By refluxing **1a–1e** with ethyl bromoacetate in the refluxing system of K_2CO_3/acetone for a relatively long time (5–7 days), the fully alkylated products **3a–3d** were obtained in lower yield (11%–27%). But no alkylated product can be separated from the alkyation reaction of ferrocenyl pyrogallol[4]arene **1e**, which might be due to the much lower solubility of **1e** in acetone. The try of carrying out the alkylation of **1e** in other solvents such as acetonitrile,



Scheme 1

DMF and in higher reaction temperature do not make any progress. **3a–3d** have twelve ethoxycarbonylmethoxy groups and are also very soluble in common organic solvents. The structure of all ester products was characterized by ^{1}H NMR and IR spectroscopy. In their IR spectra, the C=O stretching frequency usually exhibits at 1750 cm^{-1}. In ^{1}H NMR spectroscopy, the -OCH_2CO- group usually has broad peak at about 4.30–4.50 ppm besides other character peak of each group.

X-ray single crystal structure analysis was carried out for crystals of **2a** and **2e** which were obtained by crystallization from EtOH/$CHCl_3$. The crystal and structure refinement data are given in Table 1. The molecular structures of **2a** and **2e** are shown in Figs. 1 and 2. Form the Figure it can be seen that there are twelve actyl groups in **2a** and **2e** which uniquely confirmed the structures of the aryl pyrogallol[4]arenes. Generally resorcianrene and pyrogallol[4]arene show two preferred configurations (all-*cis* (*rccc)* and *cis-trans-trans (rctt)* configurations). It is interesting to find that phenylpyrogallol[4]arene **2a** is *rctt* (*cis-trans-trans*) isomer (Fig. 1). The four pyrogallol units in the ring were divided into two groups with two pyrogallol rings at almost perpendicular direction and other two pyrogallol rings are nearly in horizontal. The stretching direction of two perpendicular pyrogallol rings is opposite. One is upper standing and the other is upside down. The four side phenyl groups are also divided into two groups, with two neighbouring phenyl groups at C1 and C20, locating in upper direction, while other two phenyl groups at C13 and C32 stretching to the down direction.

It can be seen that **f**errocenyl pyrogallol[4]arene **2e** is *rccc* (all *cis*) configuration isomer (Fig. 2). The four side ferrocenyl groups stretch to one direction in the crystal, which is similar to the configuration of ferrrocenyl resorcinarene [27]. The four pyrogallol units in the ring is also divided into two groups with two pyrogallol rings being perpendicular to other two pyrogallol rings. It is different from that of **2a** in which the stretching direction of two perpendicular pyrogallol rings of **2e** is in one direction.

Ferrocenyl pyrogallol[4]arene **2e** represents that the multi-redox active ferrocenyl groups were firstly introduced in pyrogallol[4]arene. It is interesting to study its electrochemical properties. Cyclic voltammetric (CV) studies on **2e** were carried out in CH_2Cl_2 solutions (Glass-

Table 1 Crystal data and structure refinement details of **2a** and **2e**

Crystal data	**2a**	**2e**
Empirical formula	$C_{76}H_{64}O_{24}$	$C_{92}H_{80}O_{24}Fe_4{\cdot}2CHCl_3{\cdot}3H_2O$
Formula weight	1361.27	2085.82
Crystal size (mm)	0.30 × 0.20 × 0.20	0.40 × 0.32 × 0.20
Color	Colorless	Yellow
Crystal system, space group	Monoclinic, P2(1)/n	Monoclinic, P2(1)/n
a (Å)	15.7736(6)	17.3780(12)
b (Å)	13.5498(5)	4.6126(10)
c (Å)	18.0397(7)	38.267(3)
α (°)	90	90
β (°)	92.378(3)	99.4140(10)
γ (°)	90	90
Volume (Å^3)	3852.3(3)	9586.5(12)
Z	2	4
Calculated density (g cm^{-3})	1.174	1.441
F(000)	1695	4272
Temperature (K)	298(2)	273(2)
Reflections collected/unique	5307/2864	48941/16858
R(int)	0.0472	0.0565
Data/restraints/parameters	2864/0/458	16858/9/1192
θ range (°)	1.98–24.97	2.02–25.00
Absorption coefficient (mm^{-1})	0.131	0.836
Refinement method	Full-matrix-least-squares on F^2	Full-matrix-least-squares on F^2
Goodness-of-fit on F^2	1.147	1.063
R [I > 2σ (I)]	0.1821	0.1417
wR2	0.3193	0.2487
Extinction coefficient	0.017(4)	—
Largest diff. peak and hole(e Å^{-3})	1.301 and −0.302	0.927 and −1.013

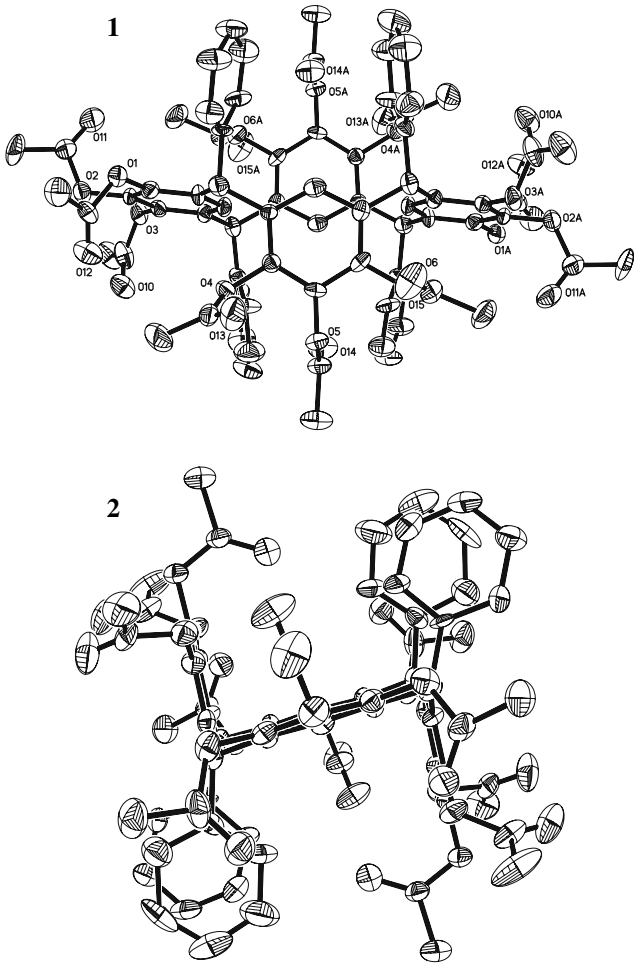


Fig. 1 Crystal structure of **2a** (1) and side view (2). Hydrogen atoms are omitted. Displacement ellipsoids are drawn at the 25% probability level

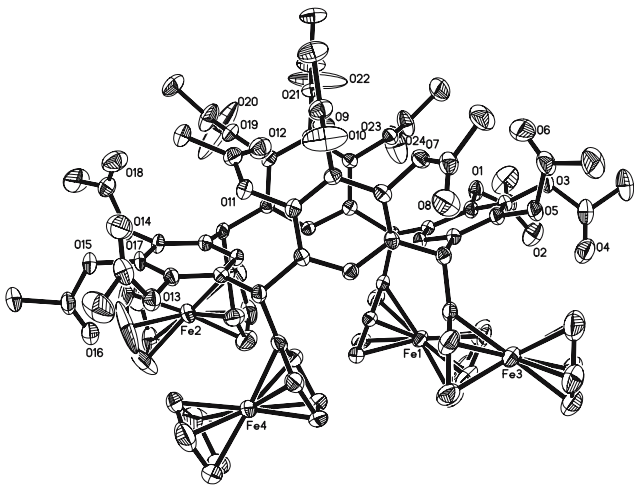


Fig. 2 Crystal structure of **2e**. Hydrogen atoms are omitted. Displacement ellipsoids are drawn at the 25% probability level

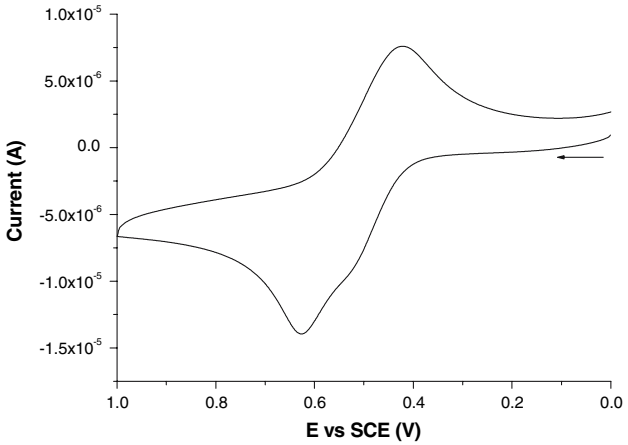


Fig. 3 Cyclic voltammetric curves (5×10^{-4} M CH_2Cl_2 solution, 0.1 M Bu_4NClO_4(TBAP), 298 K; scan rate 50 mV s^{-1}) for **2e**. Scan range: 0–1.0 V

carbon anode, 0.1 M $Bu_4N^+ClO_4^-$ as the supporting electrolyte) which produced a single redox wave with an $E_{1/2}$ value of 0.52 V (versus SCE; scan rate 50 mV/s) indicating that all four ferrocenyl units of **2e** were essentially electronically equivalent and underwent independent reversible one-electron transfer at the same potential (Fig. 3). On the other hand, the $E_{1/2}$ value of **2e** is nearly equal to the data of ferrocene (E_{pa} = 0.548 V, E_{pc} = 0.441 V, $E_{1/2}$ = 0.494 V), which means the benzyl groups have weak electron donating ability.

Experimental

Materials and apparatus

Melting points were taken on a hot-plate microscope apparatus and were uncorrected. ^{1}H NMR spectra were recorded with a Bruker AV-600 spectrophotometer (600 MHz for ^{1}H NMR). IR spectra were obtained on a Bruker Tensor 27 spectrometer (KBr disc). Elemental analysis was obtained on Perkin Elemer 2400 SERIES II Instrument. X-ray data were collected on a Bruker Smart APEX-2 diffractometer. The Cyclic Voltammograms were recorded with a Shanghai ZhenHua CHI 660 A recorder.

All reagents (pyrogallol, benzaldehyde, ethyl, ethyl α-bromoacetate,) and solvents (acetone, chloroform, dichloromethane, dimethyl sulphoxide, alcohol and ether) are commercial reagents with analytical grade and used as received. Further purification and drying by standard method were employed and distilled prior to use when necessary. Ferrocenecarbaldehyde were prepared according to the literature methods. The plates used for thin-layer chromatography (TLC) were silica gel GF_{254} (0.25 mm

thickness) precoated on glass plates flash column chromatograph was performed on silica gel H.

General procedure for the synthesis of aryl pyrogallol[4]arenes

Pyrogallol (10 mmol, 1.26 g) and aromatic aldehyde (10 mmol) was dissolved in 30 mL of ethanol under a N_2 atmosphere (**Scheme** 1). The solution was stirred at 0 °C and the concentrated hydrochloric acid (10 mL) wadded. The reaction mixture was then heated to 70–80 °C for 6 h. The precipitate was filtered and washed with water, ethanol to give pink solids **1a–1d** (63–85%) and dark red solid **1e** (89%) (**Scheme** 1).

General procedure for the synthesis of acylated aryl pyrogallol[4]arenes

A mixture of pyrogallol[4]arene **1a–1e** (1.0 mmol), 15 mL acetic anhydride and 0.3 mL pyridine as a base was refluxed for 8 h. After cooling water was added and the mixture was extracted with chloroform and dried with Na_2SO_4. Evaporation of the solvent gives colorless or yellow solid, which was purified by gel permeation chromatography (GPC) with chloroform and ethyl acetate (V/V = 1/3). **2a**: 47.8%, mp > 250 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 6.96–7.04 (m, 12H, ArH); 6.77–6.83 (m, 8H, ArH); 6.28 (s, 4H, ArH); 5.98 (s, 4H, CH); 1.94–2.19 (m, 36H, $COCH_3$) ppm. IR(KBr): 1780 (vs), 1428 (m), 1372 (s), 1203 (vs), 1041 (s), 900 (w), 872 (w), 696 (m) [cm^{-1}]. Calcd for $C_{76}H_{64}O_{24}$: C 67.05, H 4.74; found: C 66.90, H 4.61.

2b: 43.1%. mp > 250 °C. ^{1}H NMR($CDCl_3$) δ: 6.83–6.84 (m, 8H, ArH); 6.64(s, 8H, ArH); 6.24 (s, 4H, ArH); 6.04 (s, 4H, CH), 2.23–2.25 (br, 12H, $ArCH_3$); 1.97–2.17 (m, 36H, $COCH_3$) ppm. IR(KBr) υ: 1789 (vs), 1778 (vs), 1442 (s),; 1280 (s), 1210 (s), 1198 (vs), 1083 (m)[cm^{-1}].; Anal. calcd. $C_{80}H_{72}O_{24}$: C 67.78, H 5.12; found C 68.01, H 5.24.

2c: 29.7%. mp > 250 °C. ^{1}H NMR($CDCl_3$) δ: 6.60–6.67 (m, 16H, ArH); 6.21 (br, 4H, ArH); 5.93 (s, 4H, CH); 3.75 (s, 12H, OCH_3); 1.99–2.36 (m, 36H, $COCH_3$) ppm. IR (KBr) υ: 1773 (vs), 1604 (w), 1504 (s), 1435 (m), 1365 (m), 1254 (m), 1196 (vs), 1168 (s), 1153 (s), 1069 (m), 1027 (m)[cm^{-1}]; alcd. $C_{80}H_{72}O_{28}$: C 64.86, H 4.90; found C 65.06, H 4.98.

2d: 35.4%. mp > 250 °C. ^{1}H NMR($CDCl_3$) δ: 6.60–6.72 (m, 16H, ArH); 6.19 (s, 4H, ArH); 5.88 (s, 4H, CH); 2.01–2.27 (m, 36H, $COCH_3$) ppm. IR (KBr) υ: 1780 (vs), 1485 (w), 1435 (m), 1365 (m), 1196 (vs), 1168 (s), 1153 (s), 1027 (m) [cm^{-1}]. Anal. calcd. $C_{76}H_{60}O_{24}Cl_4$: C 60.89, H 4.03; found C 60.71, H 4.12.

2e: 10.5%. mp > 250 °C. ^{1}H NMR(600 MHz, $CDCl_3$) δ: 6.31 (s, 4H, ArH); 5.08 (s, 4H, CH); 4.15 (br, 36H, C_5H_4 and Cp); 2.16 (m, 36H, $COCH_3$) ppm. IR(KBr): 1784 (COO) [cm^{-1}]. Anal. calcd for $C_{92}H_{80}O_{24}Fe_4 2CHCl_3$ $3H_2O$: C 54.13%, H 4.25%; found: C 53.94%, H 4.18%.

General procedure for alkylation of aryl pyrogallol[4]arenes

A suspension of **1a–1d** (1.0 mmol) and anhydrous potassium carbonate (50 mmol, 6.90 g), potassium iodide (0.5 g, 3.0 mmol) in dry acetone (60 mL) was heated to reflux under nitrogen for at least 0.5 h. Then ethyl α-bromoacetate (18 mmol, 2.7 mL) was added. The reaction mixture was refluxed for 7 days. After removal of acetone, the residue was dissolved in water and acidified with hydrochloride acid, then extracted with $CHCl_3$. The yellow organic layers were separated and dried with $MgSO_4$. Evaporation of the solvent gives red oil residure. Titrated with alcohol to give yellow crude products, which were recrystallized from alcohol to give white solid of **3a** (27.1%). mp 129–131 °C. ^{1}H NMR($CDCl_3$) δ: 6.94–6.99 (m, 12H, ArH); 6.66–6.67 (m, 8H, ArH); 6.12 (s, 4H, ArH); 5.96 (s, 4H, CH); 4.42–4.54 (m, 24H, OCH_2); 4.02–4.18 (m, 24H, OCH_2CO); 1.19–1.39 (m, 36H, CH_3) ppm. IR (KBr) υ: 1766 (vs), 1731 (s), 1604 (w), 1442 (s), 1379 (m), 1287 (m), 1210 (s), 1090 (s), 1055 (m), 703 (m) [cm^{-1}]. Anal. calcd. $C_{100}H_{112}O_{36}$: C 63.55, H 5.97; found C 63.25, H 5.71.

3b: 20.1%. mp 178–180 °C. ^{1}H NMR($CDCl_3$) δ: 6.64–6.72 (m, 16H, ArH); 6.14 (s, 4H, ArH); 5.82 (s, 4H, CH); 4.24–4.32 (m, 24H, OCH_2); 4.09–4.20 (m, 24H, OCH_2CO); 2.24–2.28 (s, 12H, $ArCH_3$); 1.13–1.39 (m, 36H, CH_3) ppm. IR(KBr) υ: 1752 (vs), 1442 (s), 1280 (m), 1210 (s), 1083 (s) [cm^{-1}]. Anal. calcd. $C_{104}H_{120}O_{36}$: C 64.19, H 6.22; found C 64.34, H 5.98.

3c: 24.2%. mp 177–179 °C. ^{1}H NMR($CDCl_3$) δ: 6.57–6.62 (m, 16H, ArH); 6.08–6.09(m, 4H, ArH); 5.93 (s, 4H, CH); 4.25–4.30 (m, 24H, OCH_2); 4.10–4.20 (m, 24H, OCH_2CO); 1.18–1.37 (m, 36H, CH_3) ppm. IR(KBr) υ: 1766 (vs), 1611 (m), 1583 (w), 1513 (s), 1470 (s), 1428 (s), 1386 (m), 1252 (s) [cm^{-1}]. Anal. calcd. $C_{104}H_{120}O_{40}$: C 62.14, H 6.02; found C 62.30, H 5.86.

3d: 11.4%. mp 173–175 °C. ^{1}H NMR($CDCl_3$) δ: 6.81–6.82 (m, 8H, ArH); 6.68–6.70 (m, 8H, ArH); 6.08 (s, 4H, ArH); 5.97 (s, 4H, CH); 4.25–4.52 (m, 24H, OCH_2); 4.11–4.19 (m, 24H, OCH_2CO); 1.16–1.32 (m, 36H, CH_3) ppm. IR(KBr) υ: 1766 (vs), 1609 (m), 1470 (m), 1422 (m), 1203 (vs), 1111 (m), 1083 (s), 1027 (m) [cm^{-1}]. Anal. calcd. $C_{100}H_{108}O_{36}Cl_4$: C 59.23, H 5.37; found C 59.03, H 5.51.

Single crystal X-ray analysis

Crystal of compounds **2a** and **2e** suitable for single-crystal X-ray diffraction were grown by slow evaporation of a mixed solution of chloroform and ethanol.

X-ray data were collected at 293(2) K on a Bruker Smart APEX-2 diffractometer using Mo Ka X-ray (λ = 0.71073 Å) source and a graphite monochromator. The unit cell dimensions were obtained from a least-square fit to setting angles of 25 reflections. Psi scan absorption corrections were applied. The structures were solved by direct methods and refined by full-matrix least square method using SHELXL97. In the final step of refinement procedure, all non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen thermal displacement parameters were fixed at 1.2 and 1.5 times the equivalent isotropic thermal displacement parameters of their internal and terminal carrier atoms, respectively. A summary of crystallographic relevant data is given in Table 1.

Conclusion

In sum, Aryl and ferrocenyl pyrogallol[4]arenes have been conveniently synthesized in high yields by the HCl-catalyzed condensation of pyrogallol with aromatic aldehydes and ferrocenecarbaldehyde. The fully acetyl and ethoxycarbonylmethoxy derivatives were also prepared by the acetylation with acetic anhydride or alkylation with ethyl bromoacetate, which help to confirm the structures of pyrogallol[4]arenes. The crystal structure of the fully acylated phenyl pyrogallol[4]arene existed in *rctt* isomer, while the corresponding ferrocenyl pyrogallol[4]arene in *rccc* isomer. This information will be useful to further design the supramolecular system based on pyrogallol[4]arenes.

Supplement

Crystallographic data (CCDC-617135 for **2a**, CCDC-617136 for **2e**) have been deposited at the Cambridge Crystallographic Database Centre and is available on request from the Director, CCDC, 12 Union Road, Cambridge, CB21EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www:http//www.ccdc.cam.ac.uk)

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