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ORIGINAL ARTICLE

Synthesis, crystal structure and configuration of resorcinarene amides

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Abstract Multi-functional carbamoyloxyl groups were introduced on the outer periphery of tetraaryl and tetraferrocenyl resorcinarenes by two practical synthetic procedures. The first one is direct alkylation of phenolic hydroxyl groups of resorcinarenes with *N*,*N*-dialkyl-α-chloroacetamide in the system of K_2CO_3/KI/acetone. The second one is aminolysis of ester derivatives of resorcinarenes with excess amine such as dimethylamine and butylamine. Determined by the single crystal structures these resorcinarene amides usually show *rctt* (*cis–trans–trans*) and *rccc* (*all-cis*) configuration. The electrochemical properties of ferrocenyl resorcinarenes amides were also studied by cyclic voltammetry.

Keywords Resorcinarene · Alkylation · Aminolysis · Ferrocene · Configuration · Crystal structure · Electrochemistry

Introduction

Resorcinarenes are unique three-dimensional cyclic aromatic tetramers which are easily synthesized by well-established one-pot procedures [1, 2]. They have also attracted much interest in the field of supramolecular chemistry as artificial receptors and building blocks for even larger supramolecular architectures assemblies such as cages, capsules, and as starting materials for the preparation of more sophisticated molecules such as cavitands, carceplexes, hemicarceplexes [3–5]. Due to their structural features they also play an important role as host molecules for a variety of neutral and charged guest compounds [6, 7]. In the past decades most of such work are concentrated on the tetraalkyl resorcinarenes and their derivatives, while the study of tetraaryl reosorcinarnes, which can be derived from acid catalytic condensation aromatic aldehydes with resorcinol in ethanol, has attracted very little attention [8–10]. This phenomenon might partially be attributed to aryl resorciarenes usually having much poor solubility in common organic solvents and thus are difficulty for chemical modification and to be used as building blocks [11]. On the other hand introduction of relative rigid aryl groups on resrocinarene might make resorcinarene in more stable conformation and special three-dimensional arrangement with some interesting complexing properties, and hence, with different potential applications as molecular scaffolds and building blocks in host-guest chemistry. Recently there have been several reports about using aryl and ferrocenyl resorcinarene as host molecules [12–14]. In order to design new types of valuable receptor molecules and supramolecular structures, various methods have been developed for complete and selective modification on the upper rim and lower rim of resorcinarenes. We initiated a study on the possibility of introduction nitrogen-containing functional groups to aryl resorcinarenes, which can be potentially used in supramolecular chemistry as host-molecules for different kinds of guest-molecules [15–18] and here we want to report our research results of synthesis, crystal structures, configuration and electrochemical properties of aryl resorcinarene amide derivatives.

Experimental section

Materials and apparatus

All reagents and solvents were commercial available with analytical grade and used as received. All evaporations of

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organic solvents were carried out with a rotary evaporator in conjunction with a water aspirator. The TLC plates used for thin-layer chromatography (TLC) were silica gel GF254 (0.25 mm thickness) precoated on glass plates, and they were visualized under both long (365 nm) and short (254 nm) UV light. Tetra-*n*-butylammonium perchlorate (TBAP) was prepared by treatment of tetra-*n*-butylammonium bromide, and recrystallized three times from ethanol and dried under vacuum for 24 h. Resorcinarenes **1a–1c** [15], ethyl resorcinarylacetates **2a–2c** [18], ferrocenecarboxaldehyde [19], *N,N*-dialkyl-α-chloroacetamides [20] were prepared according to the published methods.

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). They were carried out at room temperature in deuterated trichloromethane solution unless otherwise stated. IR spectra were obtained on a Bruker Tensor27 spectrometer (KBr disc). Elemental analysis was obtained on Perkin Elemer 2400 SERIESII Instrument. X-ray data were collected on a Bruker Smart APEX-2 diffractometer. The Cyclic Voltammograms were recorded with a Shanghai ZhenHua CHI 660A recorder.

Alkylation reactions of tetraarylresorcinarene with α-chloroacetamide

A suspension of resorcinarene **1a–1c** (3.0 mmol) and anhydrous potassium carbonate (100 mmol, 13.8 g), potassium iodide (3.0 mmol, 0.5 g) in dry acetone (60 mL) was heated to refluxing under nitrogen for at least 1 h. Then *N,N*-dialkyl-α-chloroacetamide (40.0 mmol) was added and the reaction mixture was refluxed for 5–7 days. After removal of acetone, the residue was dissolved in water and acidified with hydrochloride acid, then extracted with $CHCl_3$. The organic layers were separated and dried with $MgSO_4$. After evaporation of the solvent the red residue was treated with alcohol to give yellow crude product, which was recrystallized from alcohol to give the pure product for analysis.

3a: 42.2%. mp: 220–221 °C; IR (KBr) υ: 3482(m), 2975(m), 1645(vs), 1500(m), 1460(m), 1290(m), 1195(m), 1098(m), 1040(m), 931(w) cm^{-1}. ^{1}H NMR ($CDCl_3$) δ: 6.31–6.90 (m, 28H, ArH), 5.81 (s, 4H, ArCH), 4.34–4.46 (m, 16H, OCH_2), 2.83–3.32 (m, 32H, NCH_2), 0.82–1.09 (m, 48H, CH_3) ppm. Anal. calcd. for $C_{100}H_{128}N_8O_{16}$: C 70.73, H 7.60, N 6.60; found C 70.36, H 7.32, N 6.55.

3b: 60.0%. mp: 125–126 °C; IR (KBr) υ: 3440(m), 2972(m), 1644(vs), 1508(m), 1381(m), 1300(m), 1194(m), 1099(m), 798(w) cm^{-1}. ^{1}H NMR (DMSO-d_8) δ: 6.28–6.58 (m, 24H, ArH), 5.66 (s, 4H, ArCH), 4.61 (s, 8H, OCH_2), 4.40–4.47 (m, 16H, OCH_2), 2.98–3.26 (m, 48H, NCH_2), 0.84–1.14 (m, 72H, CH_3) ppm. Anal. calcd. for $C_{124}H_{172}N_{12}O_{24}$: C 67.25, H 7.83, N 7.59; found C 66.98, H 7.78, N 7.45.

3c: 55.0%. mp: 208 °C. IR (KBr) υ: 3425(w), 2972(m), 1654(vs), 1497(s), 1265(m), 1145(m), 873(w), 493(w) cm^{-1}. ^{1}H NMR ($CDCl_3$) δ: 6.45 (s, 8H, ArH), 5.62 (s, 4H, ArCHAr), 4.92 (s, 16H, OCH_2), 4.07 (s, 8H, C_5H_4), 3.95 (s, 20H, Cp), 3.81 (s, 8H, C_5H_4), 1.26–1.30 (m, 32H, CH_2), 1.06–1.15 (m, 48H, CH_3) ppm. Anal. calcd. for $C_{116}H_{144}Fe_4N_8O_{16}$: C 65.42, H 6.82, N 5.26; found C 65.78, H 7.13, N 5.27.

3d: 62.0%; mp: 215–217 °C; IR (KBr) υ: 3450(w), 2964(s), 2929(m), 2873(w), 1654(vs), 1499(s), 1436(m), 1295(m), 1196(m), 1105(s), 1069(m), 929(m) cm^{-1}. ^{1}H NMR ($CDCl_3$) δ: 7.16 (m, 8H, NH); 6.32–6.81 (m, 28H, ArH); 5.78–5.80 (m, 4H, Ar-CH); 4.40 (s, 16H, OCH_2); 3.01–3.31 (m, 32H, NCH_2); 1.67–1.81 (m, 32H, CH_2); 0.89–1.00 (m, 48H, CH_3) ppm. Anal. calcd. $C_{116}H_{160}N_8O_{16}$: C 72.47, H 8.39, N 5.83; found C 72.15, H 8.24, N 5.44.

3e: 59.7%. mp 114–116 °C; IR (KBr) υ: 3476(m), 3415(m), 2924(w), 1676(vs), 1616(w), 1594(m), 1495(vs), 1450(w), 1400(m), 1288(m), 1193(w), 1032(w), 999(w) cm^{-1}. ^{1}H NMR ($CDCl_3$) δ: 7.22–7.31 (m, 32H, ArH), 6.98 (s, 8H, ArH), 6.76 (s, 4H, ArH), 6.61 (s, 8H, ArH), 6.24–6.35 (m, 16H, ArH), 5.27 (s, 4H, ArCH), 3.91–4.21 (m, 16H, OCH_2), 3.20–3.31 (m, 24H, NCH_3) ppm. Anal. calcd. $C_{124}H_{112}N_8O_{16}$: C 75.59, H 5.73, N 5.69; found C 75.25, H 5.62, N 5.55.

3f: 73.7%. mp 106–108 °C; IR (KBr) υ: 3475(m), 3059(w), 2925(w), 1677(vs), 1593(s), 1496(vs), 1442(m), 1393(m), 1289(m), 1179(w), 1105(w), 1033(w), 924(w) cm^{-1}. ^{1}H NMR ($CDCl_3$) δ: 7.36–7.45 (d, 24H, ArH), 7.13–7.19 (m, 28H, ArH), 6.98 (s, 8H, ArH), 6.10–6.21 (d, 24H, ArH), 5.29 (s, 4H, ArCH), 4.26 (s, 8H, OCH_2), 3.98–4.08 (m, 16H, OCH_2), 3.19–3.34 (t, 36H, N-CH_3) ppm. Anal. calcd. $C_{160}H_{148}N_{12}O_{24}$: C 73.27, H 5.69, N 6.41; found C 73.01, H 5.52, N 6.50.

3g: 86.5%, mp: 243–245 °C, IR (KBr) υ: 3401(s), 3316(w), 3063(w), 3028(w), 2971(w), 2922(w), 1682(vs), 1529(s), 1499(vs), 1450(m), 1295(m), 1196(m), 1098(s), 1055(m), 936(m) cm^{-1}. ^{1}H NMR (DMSO-d_6) δ: 7.16–7.34 (m, 40H, ArH); 6.88–6.91 (m, 8H, NH); 6.68–6.91 (m, 28H, Ar-H); 5.70–5.74 (m, 4H, Ar-CH); 4.23–4.33 (m, 16H, OCH_2); 4.02–4.11(m, 8H, CH); 1.21–1.65 (m, 24H, CH_3) ppm. ^{13}C NMR ($CDCl_3$): δ 162.0, 160.3, 155.7, 152.1, 151.3, 148.3, 148.1, 141.1, 140.5, 140.2, 135.7, 134.9, 134.8, 126.0, 125.9, 125.7, 123.8, 123.5, 122.9, 120.8, 120.0, 25.0, 13.7, 13.4 ppm. Anal. calcd. $C_{132}H_{120}N_8O_{16}$: C 76.43, H 5.83, N 5.40; found C 76.71, H 5.37, N 5.44.

Aminolysis reactions of ethyl resorcinarylacetate with amines

A mixture of ethyl resorcinarylacetate **2a–2c** (1.0 mmol) and amines (30.0 mmol) in ethanol (15 mL) and toluene

(15 mL) was refluxed for 24 h. The organic solvent and excess of amine were removed in vacuum. The residue was crystallized from ethanol to give amide as white solid.

3h: 65.0%, mp >250 °C. IR (KBr) υ: 3402(s), 2958(s), 2932(s), 2871(m), 1686(vs), 1610(w), 1584(w), 1537(m), 1507(m), 1440(m), 1302(m), 1247(m), 1199(m), 1103(m), 1056(m), 937(w), 860(w) cm^{-1}. ^1H NMR ($CDCl_3$) δ: 6.72 (s, 4H, NH), 6.62 (s, 8H, NH), 6.05–6.53 (m, 24H, ArH), 5.71 (br, 4H, ArCHAr), 4.35–4.40 (m, 16H, OCH_2), 4.23 (s, 8H, OCH_2), 3.37 (s, 8H, NCH_2), 3.08–3.21 (m, 8H, NCH_2), 2.93 (s, 8H, NCH_2), 1.57 (s, 8H, CH_2), 1.37 (s, 8H, CH_2), 1.18–1.29 (m, 32H, CH_2), 0.95 (s, 12H, CH_3), 0.82–0.85 (m, 24H, CH_3) ppm. ^{13}C NMR ($CDCl_3$) δ: 167.2, 166.7, 166.4, 156.3, 154.0, 153.5, 134.1, 129.6, 129.5, 125.1, 114.9, 125.6, 67.9, 67.7, 42.5, 39.0, 38.8, 31.9, 31.6, 20.9, 20.1, 20.0, 13.8, 13.7 ppm. Anal. calcd. for $C_{124}H_{172}N_{12}O_{24}$: C 67.25, H 7.83, N 7.59; found C 67.54, H 7.55, N 7.31.

3i: 52.0%, mp 176–178 °C. IR (KBr) υ: 3419(s), (w), 1664(vs), 1499(m), 1442(w), 1408(w), 1386(w), 1287(m), 1189(m), 1102(m), 1045(m), 812(w) cm^{-1} 672(m). ^1H NMR (DMSO) δ: 7.63 (br, 8H, NH), 6.24 (s, 8H, ArH), 5.60 (s, 4H, ArCHAr), 4.53 (s, 16H, OCH_2), 4.05 (s, 8H, C_5H_4), 3.98 (s, 8H, C_5H_4), 3.84–3.87 (s, 20H, Cp), 2.69 (s, 24H, CH_3) ppm. ^{13}C NMR ($CDCl_3$) δ 168.8(C=O), 153.4 (CH_2), 129.5, 127.0 (aryl C), 91.7 (ferrocenyl C, *ipso*), 68.8, 68.6, 68.4, 67.8 (ferrocenyl C), 35.1 (CH), 25.9 (CH_3), ppm. Anal. calcd. for $C_{92}H_{96}Fe_4N_8O_{16}$: C 61.62, H 5.40, N 6.25; found C 61.47, H 5.39, N 5.12.

3j: 55.0%, mp 180–182 °C. IR (KBr) υ: 3407(m), 2957(m), 2931(m), 1668(vs), 1539(m), 1499(m), 1440(w), 1289(m), 1190(m), 1104(m), 1055(w), 805(w) cm^{-1}. ^1H NMR ($CDCl_3$) δ: 7.08 (br, 8H, NH), 6.20 (s, 8H, ArH), 5.37 (s, 4H, ArCHAr), 4.55 (s, 16H, OCH_2), 4.12 (s, 8H, C_5H_4), 3.79 (s, 8H, C_5H_4), 3.92 (s, 20H, Cp), 3.28 (s, 16H, CH_2), 1.55 (s, 16H, CH_2), 1.39 (s, 16H, CH_2), 0.95 (s, 24H, CH_3) ppm. ^{13}C NMR ($CDCl_3$) δ 167.9 (C=O), 153.7, 153.5, 129.92 (aryl C), 89.7 (ferrocenyl C, *ipso*), 68.6, 68.5, 68.2 (ferrocenyl C), 39.1(CH), 39.0, 36.2 (CH_2), 31.6, 20.1, 13.7(CH_3) ppm. Anal. calcd. for $C_{116}H_{144}Fe_4N_8O_{16}$: C 65.42, H 6.82, N 5.26; found C 65.61, H 6.49, N 5.54.

X-ray structure determination

The procedure of crystal structure determination for both **3f** and **3i** were the same. X-ray data were collected at 293(2) K on a Bruker diffractometer using Mo Kα X-ray (0.71069 Å) source and a graphite monochromator. The unit cell dimensions were obtained from a least-squares fit to setting angles of 25° reflections. Psi scan absorption corrections were applied. The structures were solved by direct methods using CRYSTAL STRUCTURE 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. A summary of crystallographic relevant data is given in Table 1.

Electrochemical analysis

$E_{1/2}(E_{pa})$ vs. Fc^+/Fc was estimated by cyclic voltammetric method using platinum electrode as a working electrode, platinum wire as a counter electrode, and SCE as a reference electrode, the solution (0.5 mM) dissolved in CH_2Cl_2 using 0.1 M of Bu_4NClO_4(TBAP) as a supporting electrolyte with a scan rate of 50 mV/s and all the potentials were calibrated and referenced with ferrocene ($E_{1/2}$ (Fc/Fc^+) = 0.49 V vs. SCE) as an internal standard.

Results and discussion

Synthesis and characterization

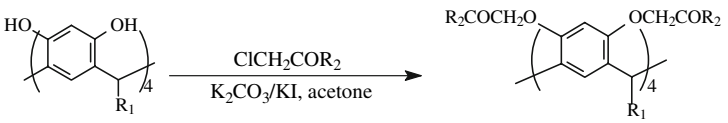
The *O*-alkylation of phenolic hydroxyl groups is the first choice for the modification at the upper rim of resorcinarenes, and have been used in a lot of alkyl resorcinarenes [21, 22]. But aryl resorcinarenes **1a–1c** (Ar = Ph, *p*-HOC_6H_5, Fc) have much lower solubility in common organic solvents such as chloroform, ethanol, acetonitrile and DMF, which caused some difficulty in basic alkylation reactions. We have showed that by refluxing of **1a–1c** with ethyl α-chloroacetate in the system of K_2CO_3/KI/acetone for relatively longer times (5–7 days), the fully alkylated resorcinarene ester products **2a–2c** can be obtained in satisfied yields [18]. In order to prepare resorcinarene amide derivatives, this direct alkylation approach could be carried out by using α-chloroacetamides as alkylating agents. Thus resorcinarenes **1a–1c** were directly alkylated with *N,N*-dialkyl-α-chloroacetamides (α-$ClCH_2CONR_2$, R_2 = Et_2, *n*-Pr_2, MePh, CH(Me)Ph) which were prepared previously from the reactions of α-chloroacetic chloride with dialkylamines. The alkylation reactions were carried out by refluxing the reactants in the system of K_2CO_3/KI/acetone for 5–7 days. After workup resorcinarenes amides **3a–3f** are prepared in moderate yields (42–86%) (Scheme 1).

The second route for the preparation of resorcinarene amide derivatives is aminolysis of the activated resorcinarene ester derivatives **2b–2c** with suitable amines. This procedure has been used in the synthesis of some inherently chiral resorcinarene amide derivatives [23–25]. Aminolysis was easily achieved by refluxing **2b–2c** in excess of liquid primary amines such as methylamine

Table 1 Crystal data and structure refinement details for **3f** and **3i**

	3f	**3i**
Empirical formula	$C_{160}H_{148}N_{12}O_{24}$	$C_{92}H_{96}Fe_4N_8O_{16}$
Formula weight	2623.00	1793.21
Crystal system, space group	Triclinic, P-1	Monoclinic, P21/c
Unit cell dimensions		
a (Å)	12.889(2)	12.968(5)
b (Å)	17.531(3)	24.154(10)
c (Å)	18.759(3)	33.495(12)
β (°)	77.895(3)	98.201(7)
Volume (Å^3)	3877.2(10)	10,384(7)
Z, Calculated density (g cm^{-3})	2, 1.287	4, 1.152
Absorption coefficient (mm^{-1})	0.189	0.607
F(0 0 0)	1,580	3,776
Crystal size (mm)	0.20 × 0.20 × 0.10	0.20 × 0.20 × 0.10
θ Range for data collection (°)	2.20–25.00	1.97–25.00
Limiting indices	$-15 \le h \le 13$, $-20 \le k \le 20$, $-22 \le l \le 19$	$-8 \le h \le 15$, $-28 \le k \le 28$, $-39 \le l \le 27$
Reflections collected/unique	20,383/13,469 [$R_{int} = 0.0735$]	42,371/17,361 [$R_{int} = 0.2165$]
Completeness (%)	98.5	94.9
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	13,469/0/961	17,361/54/491
Goodness-of-fit on F^2	0.887	1.156
Final R indices [$I > 2\sigma I$]	$R_1 = 0.0993$, $wR_2 = 0.2388$	$R_1 = 0.1997$, $wR_2 = 0.4666$
R indices (all data)	$R_1 = 0.2555$, $wR_2 = 0.3130$	$R_1 = 0.3996$, $wR_2 = 0.5280$
Largest difference peak and hole (e Å^{-3})	0.815 and −0.525	1.688 and −0.599

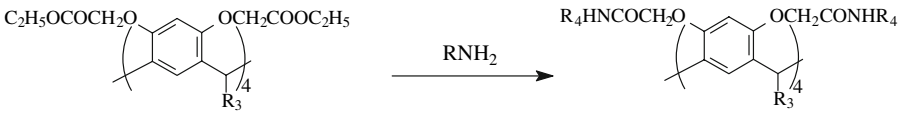
Scheme 1 The first synthetic route for resorcinarene amide



1a: R_1=Ph
1b: R_1=C_6H_4OH
1c: R_1=Fc

3a: R_1=Ph, R_2=$N(C_2H_5)_2$
3b: R_1=$C_6H_4OCH_2COR_2$, R_2=$N(C_2H_5)_2$
3c: R_1=Fc, R_2=$N(C_2H_5)_2$
3d: R_1=Ph, R_2=$N(CH_2CH_2CH_3)_2$
3e: R_1=Ph, R_2=$N(CH_3)Ph$
3f: R_1=$C_6H_4OCH_2COR_2$, R_2=$N(CH_3)Ph$
3g: R_1=Ph, R_2=$NHCH(CH_3)Ph$

Scheme 2 The second synthetic route for resorcinarene amide



2b: R_3=$C_6H_4OCH_2COOC_2H_5$
2c: R_3=Fc

3h: R_3=$C_6H_4OCH_2CONHR_4$, R_4=$(CH_2)_3CH_3$
3i: R_3=Fc, R_4=CH_3
3j: R_3=Fc, R_4=$(CH_2)_3CH_3$

hydrate, *n*-butylamine and α-phenethylamine for 24 h and resorcinarene amide derivatives can be synthesized in high yields (86–98%). These amide derivatives **3h–3j** are octopus type compounds with long soft amide chains. The structures of all amide products were characterized with ^{1}H NMR and IR spectroscopy. In their IR the C=O stretching frequency of amide groups usually exhibit at 1,647 cm^{-1}. In ^{1}H NMR spectroscopy besides other character peak of each group, the –OCH_2CO– group usually has mixed peaks at 4.30–4.50 ppm (Scheme 2).

Crystal structures

The X-ray single crystal analysis of two representative compounds **3f** and **3i** confirms the structure of the

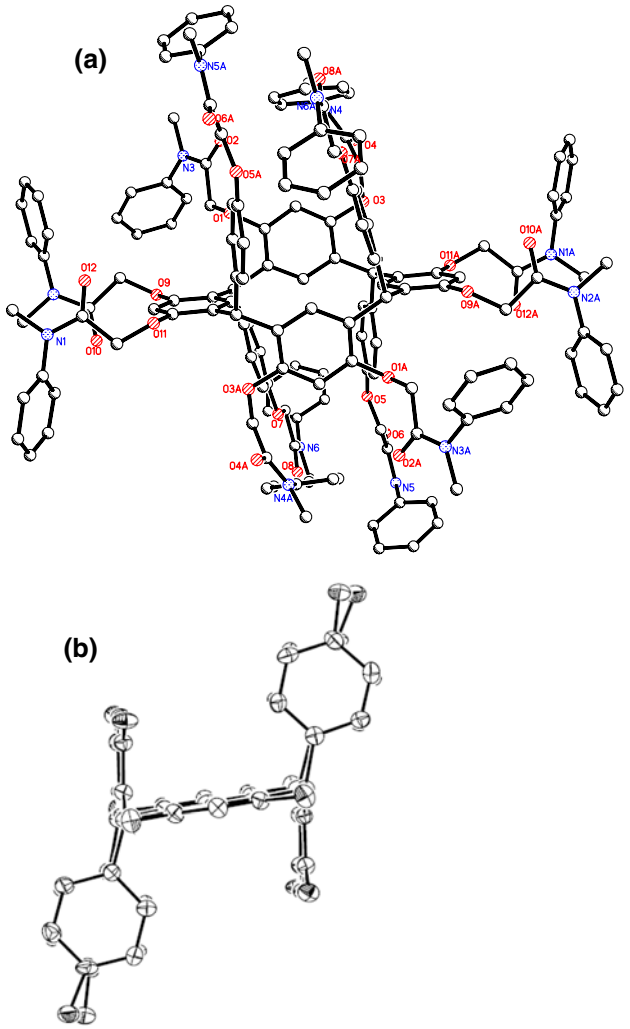


Fig. 1 (**a**) ORTEP drawing of amide **3f** with 30% probability and hydrogen atoms are omitted for clarity. (**b**) Side-view of **3f** omitted all substituted groups

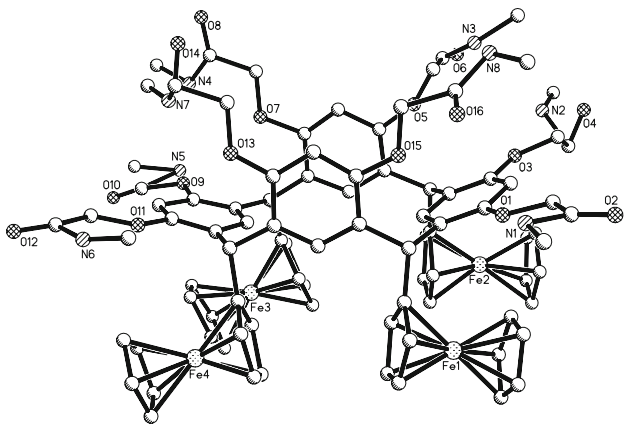


Fig. 2 ORTEP drawing of amide **3i** with 30% probability and hydrogen atoms are omitted for clarity

Table 2 Electrochemical data of **3c**, **3i**, and **3j** at scan rates 50 mV s^{-1}

Fc-e → Fc^+	Entry			
	E_{pa}[V]	E_{pc}[V]	ΔE_p[V]	$E_{1/2}$[V]
FcH	0.548	0.441	0.107	0.494
3c	0.520	0.303	0.217	0.412
3i	0.482	0.378	0.104	0.430
3j	0.513	0.368	0.145	0.441

All potentials are referred to the saturated calomel electrode (SCE) in CH_2Cl_2 solution

synthesized resorcinarene amide derivatives. Their crystal structures are shown in Figs. 1, 2 and the crystal data are listed in Table 1. From Fig. 1a it is clearly found that there are 12 *N*-methyl-*N*-phenylamino groups stretched at outer periphery, which means that both eight hydroxyl groups of resorcinol units and four hydroxyl groups of *p*-hydroxylpehnyl groups in **3f** are all alkylated. To see its structure more directly, all substituted groups are omitted (Fig. 1b). It is interesting to find that core of **3f** shows a chair conformation seeing from side-view and so it is in *rctt* (*cis–trans–trans*) configuration isomer. The four resorcinol units in the ring were divided into two groups with two resorcinol rings at almost perpendicular direction and other two resorcinol rings are nearly in horizontal. The stretching direction of two perpendicular resorcinol rings is opposite. One is upper standing and the other is upside down. The four side *p*-hydroxylphenyl groups are also divided into two groups with two neighboring phenyl groups at C1 and C20 locating in upper direction, while other two phenyl groups at C13 and C32 stretching to down direction.

From Fig. 2 it can be seen that the four ferrocenyl groups in **3i** stretch to down rim of resorcinarene and eight *N,N*-dimethylamino groups are located at upper rim. So the molecule is in *rccc* (all *cis*) configuration. All four reosocinol rings stretch to upper direction, two of them are almost vertical, and other two nearly in horizontal, which is similar to the conformation of other ferrrocenyl resorcinarene derivatives [26].

Electrochemical properties

In view of the interest in the existence of ferrocenyl linking between two aryl unites of resorcinarenes, we studied the electrochemical properties of the ferrocenyl resorcinarenes compounds **3c**, **3i**, and **3j** by cyclic voltammetry (CV). The peak potentials of the anodic and cathodic waves (E_{pa} and E_{pc}, respectively) for the oxidation processes were given in Table 2 and values were compared to that of ferrocene itself. The structure of compounds **3c**, **3i** and **3j** are similar, so they should have the similar electrochemical behavior.

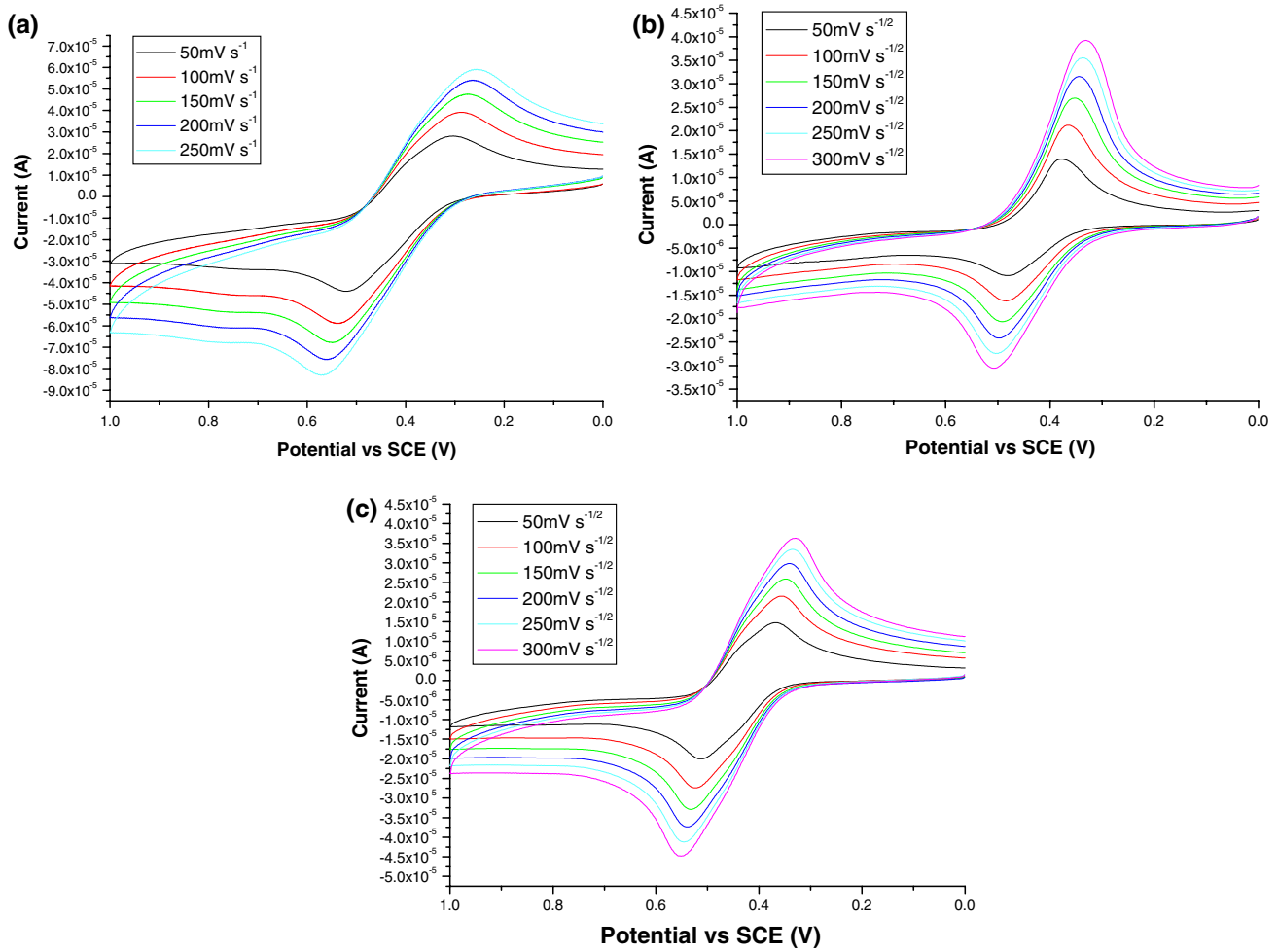


Fig. 3 Cyclic voltammetric curves (5×10^{-4} M CH_2Cl_2 solution, 0.1 M Bu_4NClO_4(TBAP), 298 K; scan rate 50 mV s^{-1}) for the ferrocene units in (**a**) **3c**, (**b**) **3i** and (**c**) **3j**

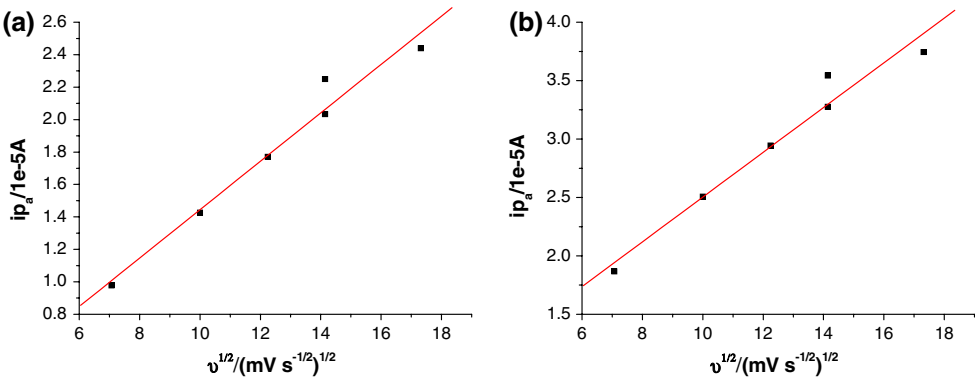


Fig. 4 The relation of i_{pa} with $v^{1/2}$ of **3i** for (**a**) and **3j** for (**b**)

In the scan range of 0–1.0 V, compounds **3c**, **3i** and **3j** show only one redox wave, which suggests that the four ferrocene groups in the resorcinarene are in nearly same environment. The peak potential of **3c**, **3i** and **3j** is +0.520 V, +0.482 V and +0.513 V, respectively, all of them are smaller than that of ferrocene (+0.548 V), which may cause by the electron-donating effect of benzyl groups. During the experiment, it was founded that few **3c** was adsorbed onto the working electrode, so the curve of **3c** shows distortion obviously, which suggests that redox process of **3c** was irreversible. But **3i** and **3j** did not show this phenomena. Furthermore, with the scan rate being larger gradually (50–300 mV s^{-1}), the i_{pa} of compounds **3i** and **3j** is linear with the square root of scan rate $v^{1/2}$((a) and

(b)), but no good linear curve for **3c** could be gotten. There exists the equation $i_p = 2.69 \times 10^{-5} n^{3/2} A D_\circ^{1/2} C_\circ^* v^{1/2}$ between peak current (i_p) and square root of scan rate ($v^{1/2}$) in reversible reactions, so i_p is direct proportional to $v^{1/2}$. Although the i_{pa} and $v^{1/2}$ of compounds **3i** and **3j** showed good linear relations, their plots do not across the zero point. In conclusion these data indicated that their redox process were irreversible and adsorption-controlled [27] (Figs. 3, 4).

Conclusion

In conclusion we have demonstrated that Multi-functional carbamoyloxyl groups can be introduced on the outer periphery of tetraaryl and tetraferrocenyl resorcinarenes by two practical synthetic procedures. The first one is direct alkylation of phenolic hydroxyl groups of resorcinarenes with *N*,*N*-dialkyl-α-chloroacetamide in the system of K_2CO_3/KI/acetone. The second one is aminolysis of activated ester derivatives of resorcinarenes with excess aliphatic amine such as dimethylamine, butylamine. Determined by the single crystal structures these resorcinarene amides usually show *rctt* (*cis–trans–trans*) and *rccc* (*all-cis*) configurations. The electrochemical properties of ferrocenyl resorcinarenes amides were also studied by cyclic voltammetry.

Supplementary material

Single crystal X-ray diffraction data are deposited with CCDC (Deposition numbers **3f**: 648789; **3i**: 648790).

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