Cyclic voltammograms of $(TTF)_7SbI_4$ were recorded in DMF/0.1 M TEAP (tetraethylammonium perchlorate) from −0.2 to +1.0 V versus an Ag/AgCl electrode. Redox potentials of TTF molecule, $(TTF)_7SbCl_4$ and $(TTF)_5(SbBr_4)_2 \cdot CH_3COCH_3$ were also examined and summarized in Table 1. The half-wave potential ($E_{1/2}$) were estimated by averaging the anodic and cathodic peak potentials. $(TTF)_7SbI_4$ exhibits two peaks at +0.41 and +0.67 V. These are assigned to TTF^+/TTF and TTF^{2+}/TTF^+ couples, respectively. The experimentally observed $E_{1/2}$ value of TTF molecule are +0.42 and +0.66 V, assigned to TTF^+/TTF and TTF^{2+}/TTF^+ couples, respectively. The voltammogram of TTF in CH_3CN solution was also reported to show two reversible redox waves at +0.33 (TFF^+/TTF) and at +0.70 V (TFF^{2+}/TTF^+) versus SCS,[12] and support the assignment in the case of the present compounds. The cyclic voltammograms were scanned several times and there was no change in the potentials, indicating that the redox couples are reversible. A redox peak attributable to antimony metal was not detected in any case.

Conclusion

$(TTF)_7SbI_4$ was prepared from TTF and SbI_3 as a result of a charge transfer from $(TTF)_n$ molecules to SbI_4^- entity. Relatively high electrical conductivity and spectroscopic properties lead to the conclusion that partially ionized TTF radical cations have stacked to form low-dimensional chains. Magnetic properties also reveal that the magnetic interstack interaction between TTF radicals is considerable. This magnetic interaction plays an important role in enhancing the electrical conductivity, and furthermore, provides a useful information to design conductive materials.

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Facile Direct *p*-Functionalization of Calix[4]arene through Transmetallation of *p*-Bromocalix[4]arene Tetrahexyl Ether

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Calixarenes have attracted many interests because of their potential diversities for host-guest complexes and enzyme mimics.[1] The diversities are attributable to the various sizes, the chemical reactivities at both rims, and even the easy conformational changes of calixarenes.

Functionalizations of calixarenes both at the phenolic oxygen (lower-rim)[2] and at the *para* postion of aromatic nucleus (upper-rim)[3-7] have been developed extensively. Particularly the functionalizations at "upper-rim" of calix[4]arene have attracted considerable attentions because the upper-rim contains a hydrophobic cavity which could be manipulated for neutral substrate recognition. Shinkai *et al.* achieved the sulfonation and nitration,[3] and Gutsche *et al.* performed modification *via* the *p*-Claisen rearrangement route[4] and *via* the *p*-quinone methide route.[5] The Parma group introduced the *p*-chloromethylation route[6] and the selective diametrical functionalization of calix[4]arene at the upper-rim.[7]

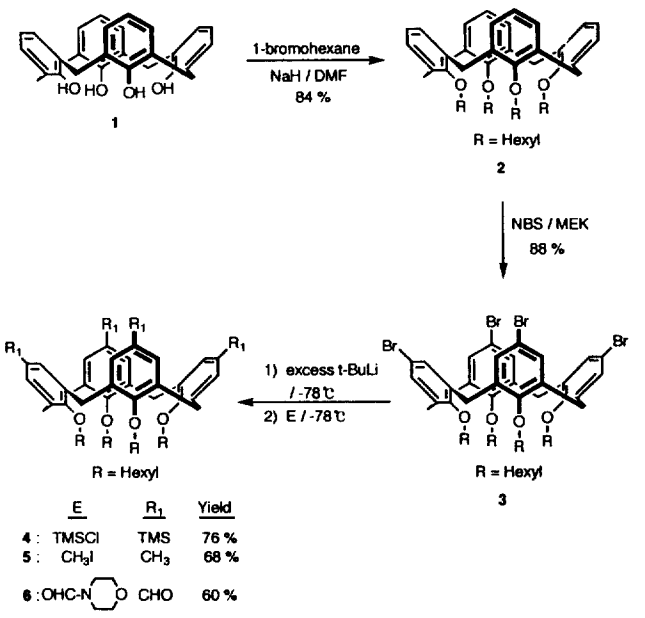
Except for Shinkai's direct electrophilic substitutions, however, one has to pass through several steps to introduce an appropriate functional group. In this respect, a direct functionalization method on the upper-rim of a common intermediate has been looked for. Indeed, transmetallation route was attempted by Gutsche *et al.*,[8] who reported the synthesis of *p*-lithiocalix[4]arene tetramethyl ether from *p*-bromocalix[4]arene tetramethyl ether by treatment with n-BuLi at −78 ℃. But, tetralithiation of *p*-bromocalix[4]arene tetrahexyl ether in the reported conditions cannot be repeated.[9] Only when the lithiate solution was warmed up to room temperature, tetralithiation was achieved in a rather low yield.

In this note we report the facile *p*-functionalization through the direct transmetallation of *p*-bromocalix[4]arene tetrahexyl ether using *t*-BuLi at −78 ℃ followed by quenching with several electrophiles.

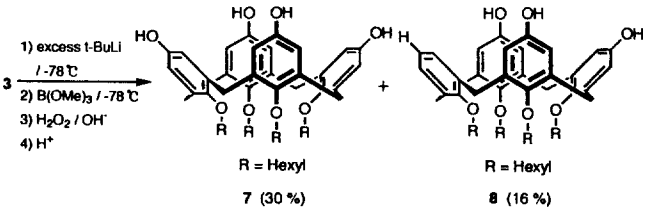
Results and Discussion

As shown in Scheme 1, alkylation of calix[4]arene **1** with 1-bromohexane afforded the fixed cone-structured tetrahexyl ether **2** in 84% yield.[10] Bromination of **2** with NBS gave *p*-bromocalix[4]arene tetrahexyl ether **3** in 88% yield.[10]

Complete metal-halide exchange of *p*-bromocalix[4]arene **3** was achieved by treatment with excess *t*-BuLi at −78 ℃ in THF for 2 h. This *p*-lithiocalix[4]arene was quenched with trimethylsilyl chloride, methyl iodide, and N-formylmorpholine to give *p*-(trimethylsilyl)calix[4]arene tetrahexyl ether **4** (76%), *p*-methylcalix[4]arene tetrahexyl ether **5** (68 %), and *p*-formylcalix[4]arene tetrahexyl ether **6** (60%) res-



Scheme 1.



Scheme 2.

pectively. The ^{1}H NMR spectra of compound **4**, **5** and **6** showed the similar patterns of a singlet for aryl protons, two doublets for the methylene bridge protons and a triplet for oxymethylene protons, which confirms the *p*-substituted cone-structured C_{4v} symmetry[11] of products.

When the *p*-lithiocalix[4]arene was quenched with trimethyl borate, oxidized with H_2O_2-NaOH and then followed by acidic hydrolysis, *p*-tetrahydroxy calix[4]arene tetrahexyl ether (tetrol **7**, 30%) and *p*-trihydroxycalix[4]arene tetrahexyl ether (triol **8**, 16%) were obtained as shown in Scheme 2. As far as we know, these *p*-hydroxycalix[4]arene cannot be obtained by any other shorter procedure.

^{1}H NMR spectrum of tetrol **7** in DMSO-d_6 gave a singlet at δ 8.50 (4H) for hydroxy protons, a sharp singlet at δ 6.15 (8H) for aromatic protons, and a triplet at δ 3.69 (8H) for oxymethylene protons. The typical two doublet pattern of the methylene bridge protons as δ 4.20 (4H, H_{endo}, J=12.6 Hz) and δ 2.90 (4H, H_{exo}, J=12.6 Hz) indicates the cone conformation of tetrol **7** in solution. ^{1}H NMR spectral patterns of triol **8** were quite different from those of tetrol **7** due to the low symmetry of **8**. ^{1}H NMR spectrum of triol **8** in $CDCl_3$ shows the distinctive aryl proton peaks of a reduced benzene unit (doublet at 7.03 ppm and triplet at 6.85 ppm), the two kinds oi bridging methylene peaks (doublets at δ 4.41, 4.36 and δ 3.08, 2.99 (J=13.5 Hz)), and the three kinds of oxymethylene peaks (triplets at 4.00, 3.92, 3.68 ppm).[12]

In conclusion, the direct *p*-functionalization of calix[4]arene was achieved by transmetallation of *p*-bromocalix[4]arene tetrahexyl ether with *t*-BuLi at −78 ℃ followed by quenching with various electrophiles. Tetrol **7** or triol **8** could be functionalized to various key intermediates useful in host-guest chemistry.[13]

Experimental Section

General Lithiation Procedure. A stirred solution of 300 mg (0.28 mmol) of the *p*-bromo compound **3** in 50 mL of anhydrous THF under argon atmosphere was cooled to −78 ℃ and treated with 4.9 mL (8.33 mmol) of 1.7 M *t*-BuLi-pentane solution dropwise. The mixture was stirred at −78 ℃ for 2 h and then quenched with a electrophile.

5,11,17,23-Tetrakis(trimethylsilyl)-25,26,27,28-tetrakis(n-hexyloxy)calix[4]arene (4). General lithiation procedure was followed except that 200 mg (0.19 mmol) of **3**, 35 mL of dry THF, and 3.3 mL (5.61 mmol) of 1.7 M *t*-BuLi were used. The lithiate was quenched with 0.8 mL (6.48 mmol) of trimethylsilyl chloride. The mixture was warmed to room temperature and stirred for 2 h. After removal of solvent under reduced pressure, the residue was extracted with ether. The organic phase was washed with water, brine and then dried over anhydrous $MgSO_4$. Column chromatography (silica, 2×11 cm, hexane) of the concentrated mixture afforded 149 mg (76%) of product: mp. 128-129 ℃; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.89 (s, 8H, Ar*H*), 4.4 (d, J=12.8 Hz, 4H, *endo*-ArC*H*), 3.89 (t, J=7.7 Hz, 8H, OCH_2), 3.17 (d, J=12.8 Hz, 4H, *exo*-ArC*H*), 2.02 (br s, 8H, OCH_2CH_2), 1.55-1.23 (m, 24H, $(CH_2)_3CH_3$), 0.93 (t, 12H, CH_3), 0.06 (s, 36H, $Si(CH_3)_3$).

5,11,17,23-Tetramethyl-25,26,27,28-tetrakis(n-hexyloxy)calix[4]arene (5). The lithiate solution was quenched with 0.6 mL (9.64 mmol) of methyl iodide. The mixture was warmed to room temperature and stirred for 2 h. After the solvent was removed under reduced pressure, the residue was extracted with ether. The organic phase was washed with water, brine and then dried over anhydrous $MgSO_4$. The solvent was evaporated and the residue was chromatographed on silica gel gravity column (2×20 cm, hexane : CH_2Cl_2=4 : 1) to yield 156 mg (68%) of product as a white powder: mp. 107.9-108.4 ℃; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.43 (s, 8H, Ar*H*), 4.38 (d, J=13.1 Hz, 4H, *endo*-ArC*H*), 3.84 (t, J=7.5 Hz, 8H, OCH_2), 3.05 (d, J=13.1 Hz, 4H, *exo*-ArC*H*), 2.06 (s, 12H, $ArCH_3$), 1.89 (br s, 8H, OCH_2CH_2), 1.54-1.25 (m, 24H, $(CH_2)_3CH_3$), 0.92 (t, 12H, CH_3); FAB$^+$ MS (thioglycerol), m/z 948 (M+Na$^+$+Matrix, 50%), 817 (M$^+$, 100%).

5,11,17,23-Tetraformyl-25,26,27,28-tetrakis(n-hexyloxy)calix[4]arene (6). The lithiate solution was quenched with 2.0 mL (19.9 mmol) of 4-formylmorpholine. The mixture was stirred at room temperature for 2 h and then acidified with 20 mL of 2 N HCl. After stirring for 1 h the solvent was removed under reduced pressure and residue was extracted with CH_2Cl_2. The organic phase was washed with water, brine and then dried over $MgSO_4$. The solution was filtered and the filtrate was concentrated. The crude mixture was chromatographed on silica gel gravity column (1.5×23 cm, hexane : EtOAc=3 : 1) to give 146 mg (60%) of product: ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.58 (s, 4H, *CH*O), 7.15 (s, 8H, Ar*H*), 4.49 (d, J=13.7 Hz, 4H, *endo*-ArC*H*), 3.96 (t, J=7.5 Hz, 8H, OCH_2), 3.35 (d, J=13.7 Hz, 4H, *exo*-ArC*H*), 1.89 (m, 8H, OCH_2CH_2), 1.37-1.25 (m, 24H, $(CH_2)_3CH_3$), 0.92

(t, 12H, CH_3).

5,11,17,23-Tetrahydroxy-25,26,27,28-tetrakis(n-hexyloxy)calix[4]arene (7) and 5,11,17-Trihydroxy-25,26,27,28-tetrakis(n-hexyloxy)calix[4]arene (8). General lithiation procedure was followed except that 1 g (0.93 mmol) of *p*-bromo compound **3**, 100 mL of dry THF, and 16.0 mL (27.2 mmol) of 1.7 M *t*-BuLi-pentane solution were used. The lithiate was quenched with 4.2 mL of $B(OMe)_3$ (36.98 mmol). The mixture was then warmed to room temperature and stirred for 2 h. After the mixture was cooled again to −78 ℃, 10 mL of 1 : 1 3 N NaOH-28% H_2O_2 solution was added and slowly warmed to room temperature. The mixture was stirred for 2 h and then 8 g of $Na_2S_2O_3 \cdot 5H_2O$ was carefully added. After stirring for 1 h, the solvent was removed under reduced pressure and then the residue was partitioned between 1 N HCl and ether. The organic phase was washed with water, brine and then dried over anhydrous $MgSO_4$. The solvent was evaporated, and the crude mixture was chromatographed on a silica gel gravity column (2.5×26 cm, hexane : EtOAc=1 : 2). The best portions of each products were collected, concentrated and then recrystallized from a mixture of acetone and hexane to give 231 mg of the tetrol **7** (30%) and 124 mg of the triol **8** (16%): Tetrol **7**: mp 267-268 ℃; ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.50 (s, 4H, O*H*), 6.15 (s, 8H, Ar*H*), 4.20 (d, *J*=12.6 Hz, 4H, *endo*-ArC*H*), 3.69 (t, *J*=7.5 Hz, 8H, OCH_2), 2.90 (d, *J*=12.6 Hz, 4H, *exo*-ArC*H*), 1.86 (br s, 8H, OCH_2CH_2), 1.33 (br s, 24H, $(CH_2)_3CH_3$), 0.90 (br s, 12H, CH_3); FAB$^+$ MS (thioglycerol), m/z 956 (M+Na$^+$+Matrix, 100%), 848 (M+Na$^+$, 40%), 825 (M$^+$, 76%); FT-IR (KBr), 3310 cm^{-1} (ν_{O-H}): Triol **8**: mp. 180.8-182 ℃; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.03 (d, *J*=6.7 Hz, 2H, H-Ar*H*), 6.85 (t, *J*=6.8 Hz, 1H, *H*-ArH), 6.53 (s, 2H, HO-Ar*H*), 6.24 (br s, 1H, O*H*), 6.07 (br s, 2H, O*H*), 5.83 (s, 2H, HO-Ar*H*), 5.68 (s, 2H, HO-Ar*H*), 4.41 (d, *J*=13.5 Hz, 2H, *endo*-ArC*H*), 4.36 (d, *J*=13.5 Hz, 2H, *endo*-ArC*H*), 4.00 (t, 2H, OCH_2), 3.92 (t, 2H, OCH_2), 3.68 (t, 4H, OCH_2), 3.08 (d, *J*=13.5 Hz, 2H, *exo*-ArC*H*), 2.99 (d, *J*=13.5 Hz, 2H, *exo*-ArC*H*), 1.90 (m, 8H, OCH_2CH_2), 1.55-1.30 (m, 24H, $(CH_2)_3CH_3$), 0.92 (m, 12H, CH_3); FAB$^+$ MS (thioglycerol), m/z 940 (M+Na$^+$+Matrix, 63%), 832 (M+Na$^+$, 56%), 809 (M$^+$, 100%); FT-IR (KBr) 3323 cm^{-1} (ν_{O-H}).

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1,2,4-Triazole Fused Heterocycles; Part 2. Preparation of 4*H*-1,2,4-Triazolo[1,5-c][1,3,5]oxadiazines

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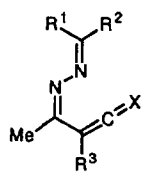
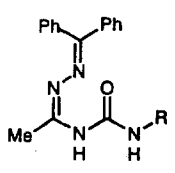
It has been shown[1,2] that cumulated azines **1** proved to be versatile synthons for a large variety of pyrazolo-fused heterocycles. Recently we reported[3] the synthesis of 5,10-dihydro-1,2,4-triazolo[5,1-*b*]quinazolines based on the dehydra-



1, X = R^4R^5C or R^4N or S



2, R = alkyl or aryl