Notes

Upper-Rim Functionalization of Calix[4]arene by Chloro(isocyanide)gold(I) Groups: An Entry to Polymetallic Architecture

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Introduction

Calix[4]arene is an important macrocyclic molecule that has attracted a lot of attention, particularly in the field of selective ion extractions and receptors.[1] Interestingly, the Cambridge Data Bank also includes numerous examples of calix[4]arene derivatives that exhibit inclusion of small organic molecules inside the cavity. Its chemical derivetizations by simple functional groups and metal-containing fragments have been reviewed by Matt et al.[2] While the lower-rim chemical manipulation has been extensively explored, including relevant works on gold(I),[3] the modification of the upper rim has been much less exhaustive. To date, connection of a limited number of functional groups on the upper-rim, such as $-SO_3^-$,[4] NO_2,[5] NH_2,[6] N═NR,[7] PPh_2,[8] and others,[9] has been performed.

This group recently reported the preparations of monoalkyl-, dialkyl-, and diarylphosphinated calix[4]arene ligands and their corresponding rhodium(I) and rhodium(III) complexes[10] and also designed numerous synthesis methodologies for the preparation of the complete series of upper-rim mono-, bi- (both isomers), tri-, and tetraphosphinated calix[4]arenes.[11] Such species will allow one to build various polynuclear complexes taking advantage of the calix[4]arene structural properties to act as a platform molecule or to provide a cavity for host−guest associations with various neutral organic molecules. The upper-rim expansion allows increase in cavity dimension with the unique opportunity of using coordinating centers for extra interactions with the substrate.

This work reports the preparation of two new ligands, the mono- and tetraisocyanocalix[4]arene, and their corresponding gold(I) chloride complexes. This metallic fragment is selected because of potential and assembling aurophilic interactions,[12] limited steric effects, and convenient luminescence properties that many gold(I) species exhibit in solutions.[13] The lower-rim is tetrapropylated to secure the cone conformation of the calix-[4]arene compounds.[14]

Experimental Section

Materials. 25,26,27,28-Tetra-*n*-propylcalix[4]arene (**1**),[15] 5-bromo-25,26,27,28-tetra-*n*-propoxycalix[4]arene (**7**),[16] 25,27-dibenzoyl-26,28-dihydroxycalix[4]arene (**13**),[11] and chloro(tetrahydrothiophene)gold(I)[17] were prepared according to literature procedures. Ethanol (94%; Fisher) was dried over sodium, made clear glasses at 77 K, and did not exhibit luminescence attributable to impurities using 250 to 350 nm excitation wavelengths. The chemical shifts with respect to TMS and coupling constants are reported in ppm and Hz, respectively.

5,11,17,23-Tetranitro-25,26,27,28-tetra-*n*-propoxycalix[4]arene (2). An 80 mL trifluoroacetic acid solution containing 25,26,27,28-tetrapropoxycalix[4]arene (**1**) (4.00 g, 6.75 mmol) was treated with $NaNO_2$ (6.50 g, 95.5 mmol). The solution was stirred for 6 h at room temperature and was poured in distilled water (300 mL). The resulting suspension was extracted twice with CH_2Cl_2 (300 mL). The organic phase was washed twiced with an aqueous solution containing Na_2CO_3 and then twice with distilled water. The organic phase was dried over $MgSO_4$, filtered, and evaporated. The resulting orange product was washed twice with MeOH. The solid was recrystalized in $CHCl_3$/CH_3OH: yield 57% (3.0 g); T_m > 300 °C; IR solid ν (cm^{-1}) 1342 (NO_2); ^1H NMR ($CDCl_3$) 7.56 (s, 8H, Ph), 4.52 (d, 4H, J = 14.0, CH_2), 3.96 (t, 8H, J = 7.5, OCH_2), 3.39 (d, 4H, J = 13.5, CH_2), 1,90 (tq, 8H, J = 7.5, CH_2CH_3), 1.02 ppm (t, 12H, J = 7.5, CH_3); ^{13}C NMR($CDCl_3$) 161.7, 142.8, 135.4, 124.0, 77.7, 31.1, 23.21, 10.1 ppm; MS (EI) *m/e* 772 (M^+). Anal. Calcd for $C_{40}H_{44}N_4O_{12}$: C, 62.17; H, 5.74; N, 7.25. Found: C, 62.18; H, 5.97; N, 7.19.

5,11,17,23-Tetraamino-25,26,27,28-tetra-*n*-propoxycalix[4]-arene (3). A THF solution (100 mL) containing compound **2** (3.0 g,

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3.9 mmol) and activated Raney Ni (1.0 g) was placed under H_2 atmosphere (69 atm, 1000 psi) for 72 h. The resulting solution was filtered to remove the catalyst and was evaporated to dryness. A white solid was obtained: yield quantitative (2.5 g); T_m = 267−269 °C; ^{1}H NMR ($CDCl_3$) 6.06 (s, 8H, Ph), 4.31 (d, 4H, J = 13,0, CH_2), 3.72 (t, 8H, OCH_2), 3.30 (br s, 8H, NH_2), 2.92 (d, 4H, J = 13.0, CH_2), 1.86 (tq, 8H, J = 7.5, CH_2CH_3), 0.94 ppm (t, 12H, J = 7.5, CH_3); ^{13}C NMR ($CDCl_3$) 150.1, 140.2, 135.6, 115.8, 76.6, 31.1, 23.1, 10.3 ppm; MS (EI) *m*/*e* 652 (M^+). Anal. Calcd for $C_{40}H_{52}N_4O_4$: C, 73.59; H, 8.03; N, 8.58. Found: C, 73.65; H, 8.09; N, 8.49.

5,11,17,23-Tetraformamino-25,26,27,28-tetra-*n*-propoxycalix[4]-arene (4). Compound **3** (1.1 g, 1.6 mmol) was dissolved in formic acid (88%, 10 mL), to which was added toluene (80 mL). The mixture was refluxed in a Dean−Stark apparatus eliminating formic acid and water. The solution was concentrated to 30 mL, and the resulting solid was filtered out and washed with toluene (10 mL): yield 90% (1.0 g); T_m > 300 °C; IR solid ν (cm^{-1}) 1661 (C═O); ^{1}H NMR (DMSO-d_6) 9.49−9.78 (m, 4H, CHO), 7.89−8.48 (m, 4H, *NH*CHO), 7.1−6.8 (m, 8H, Ph), 4.30 (d, 4H, J = 13.0, CH_2), 3.8−3.7 (m, 8H, OCH_2), 3.1 (d, 4H, J = 13.0, CH_2), 1.9−1.8 (m, 8H, CH_2CH_3), 1.0−0.9 ppm (m, 12H, CH_3); ^{13}C NMR (DMSO-d_6) 162.4, 162.2, 158.7, 153.0, 152.6, 152.4, 152.3, 151.8, 135.3, 135.0, 134.8, 134.4, 134.0, 132.5, 132.2, 132.0, 119.3, 119.1, 118.8, 118.5, 118.4, 76.3, 30.6, 22.7, 22.2, 10.4, 10.2, 10.1 ppm; MS (EI) *m*/*e* 700 (M^+). Anal. Calcd for $C_{44}H_{52}N_4O_8$: C, 75.40; H, 7.48; N, 7.99. Found: C, 75.58; H, 7.61, N, 7.91.

5,11,17,23-Tetraisocyano-25,26,27,28-tetra-*n*-propoxycalix[4]-arene (5). Compound **4** (0.24 g, 0.30 mmol) and triethylamine (0.7 mL, 4.7 mmol) were dissolved in CH_2Cl_2 (70 mL) under N_2 atmosphere. The mixture was refluxed and slowly treated with 0.2 mL of diphosgene. The solution was stirred for 16 h, then cooled, and extracted twice with a solution containing Na_2CO_3 and twice with distilled water. The organic phase was dried over $MgSO_4$ and evaporated. The resulting solid was purified by column chromatography using an ethyl acetate/CH_2Cl_2 5:95 mixture. A beige solid was obtained: yield 80% (2.6 g); T_m > 300 °C; IR solid ν (cm^{-1}) 2130 (N≡C); ^{1}H NMR ($CDCl_3$) 6.72 (s, 8H, Ph), 4.39 (d, 4H, J = 13.5, CH_2), 3.84 (t, 8H, J = 7.5, OCH_2), 3.15 (d, 4H, J = 13.5, CH_2), 1.87 (tq, 8H, CH_2CH_3), 0.98 ppm (t, 12H, J = 7.0, CH_3); ^{13}C NMR ($CDCl_3$) 164.1, 157.4, 136.2, 126.7, 121.4, 77.7, 31.2, 23.5, 10.3 ppm; MS (EI) *m*/*e* 692 (M^+). Anal. Calcd for $C_{44}H_{44}N_4O_4$: C, 76.28; H, 6.40; N, 8.08. Found: C, 76.30; H, 6.40; N, 7.81. UV−vis (EtOH) [λ_{max}/nm (ϵ/M^{-1} cm^{-1})]: 218 sh (106 000), 248 sh (43 500), 265 sh (2450).

Tetrachloro(5,11,17,23-tetraisocyano-25,26,27,28-tetra-*n*-propoxycalix[4]arene)tetragold(I) (6). A CH_2Cl_2 solution (10 mL) containing **5** (0.020 g, 0.029 mmol) was added to a CH_2Cl_2 solution (10 mL) containing $Au(SC_4H_8)(Cl)$ (37 mg, 0.12 mmol) under inert atmosphere. The resulting solution was stirred for 10 min at room temperature. A white precipitate was formed which was filtered out and washed with CH_2Cl_2: yield 95% (0.044 g); T_f > 200 °C (dec); IR solid ν (cm^{-1}) 2121 (N≡C); ^{1}H NMR ($CDCl_3$) 7.09 (s, 8H, Ph), 4.37 (d, 4H, J = 13,5, CH_2), 3.85 (t, 8H, J = 7.5, OCH_2), 3.20 (d, 4H, J = 13.5, CH_2), 1.89 (m, 8H, CH_2CH_3), 1.00 ppm (t, 12H, J = 7.5, CH_3); ^{13}C NMR ($CDCl_3$) 136.2, 128.0, 78.0, 30.7, 24.0, 10.3 ppm; MS (MALDI-TOF) *m*/*e* 1584 (100%, calix(NC)$_4$Au$_4$Cl$_3$). Anal. Calcd for $C_{44}H_{44}N_4O_4Au_4Cl_4$·0.25$C_4H_8S$: C, 32.87; H, 2.82; N, 3.41; S, 0.49. Found: C, 32.40; H, 2.57; N, 3.19; S, 0.56. UV−vis (EtOH) [λ_{max}/nm (ϵ/M^{-1} cm^{-1})]: 280 (2550).

5-Phthalimido-25,26,27,28-tetra-*n*-propoxycalix[4]arene (8). A solution containing **7** (1.5 g, 2.3 mmol), phthalimide (0.50 g, 3.4 mmol), and Cu_2O (1.6 g, 11 mmol) in collidine (50 mL) was refluxed for 2 days under inert atmosphere. The reaction mixture was cooled to room temperature and was poured in CH_2Cl_2 (700 mL). This solution was extracted twice with 5% H_2SO_4 aqueous solutions, 5% NaOH, and distilled water. The organic phase was dried over $MgSO_4$, filtered, and evaporated. The resulting white solid was purified by column chromatography using a CH_2Cl_2/hexanes 1:1 mixture: yield 59% (1.00 g); T_m > 200 °C (dec); IR solid ν (cm^{-1}) 1722 (C═O); ^{1}H NMR ($CDCl_3$) 7.9 (m, 2H, Ph phthalimide), 7.7 (m, 2H, Ph phthalimide), 6.92 (s, 2H, PhN calix), 6.79 (d, 2H, J = 7.5, Ph), 6.62 (t, 1H, J = 7.5, Ph), 6.47−6.58 (m, 6H, Ph), 4.51 (d, 2H, J = 13.5, CH_2), 4.48 (d, 2H, J = 13.5, CH_2), 3.97 (t, 2H, J = 7.5, OCH_2), 3.93 (t, 2H, J = 7.5, OCH_2), 3.82 (t, 4H, J = 7.5, OCH_2), 3.21 (d, 2H, J = 13.5, CH_2), 3.18 (d, 2H, J = 13.5, CH_2), 1.85−2.05 (m, 8H, CH_2CH_3), 0.98−1.10 ppm (m, 12H, CH_3); ^{13}C NMR 167.3, 156.9, 156.5, 156.0, 136.1, 135.5, 134.5, 134.1, 133.8, 131.8, 128.5, 128.1, 127.9, 126.0, 125.2, 123.4, 122.2, 122.0, 76.7, 76.6, 31.0, 23.3, 23.2, 10.4, 10.1 ppm; MS (EI) *m*/*e* 737 (M^+). Anal. Calcd for $C_{48}H_{51}N_1O_6$: C, 78.13; H, 6.97; N, 1.90. Found: C, 77.94; H, 6.81; N, 1.76.

5-Amino-25,26,27,28-tetra-*n*-propoxycalix[4]arene (9). A solution containing compound **8** (0.56 g, 0.76 mmol) and hydrazine monohydrate (0.37 mL, 7.6 mmol) in ethanol (50 mL) was refluxed for 2 h. The solution was cooled to room temperature and evaporated. The resulting solid was dissolved in CH_2Cl_2 (100 mL) and extracted twice with 5% NaOH aqueous solution and distilled water. The organic phase was dried over $MgSO_4$, filtered, and evaporated. The white solid purified by column chromatography using CH_2Cl_2: yield 95% (0.44 g); T_m = 209−210 °C; IR solid ν (cm^{-1}) 3362 (NH_2); ^{1}H NMR ($CDCl_3$) 6.68−6.81 (m, 9H, Ph), 6.07 (s, 2H, PhN), 4.60 (d, 2H, J = 13.5, CH_2), 4.52 (d, 2H, J = 13.5, CH_2), 3.95−4.02 (m, 6H, OCH_2), 3.90 (t, 2H, J = 7.5, NPhOCH_2), 3.29 (d, 2H, J = 13.5, CH_2), 3.17 (d, 2H, J = 13.5, CH_2), 3.16 (s, 2H, NH_2), 1.99−2.10 (m, 8H, CH_2CH_3), 1.14 (t, 3H, J = 7.5, CH_3), 1.12 ppm (t, 9H, J = 7.5, CH_3); ^{13}C NMR ($CDCl_3$) 156.5, 149.6, 140.2, 135.4, 127.9, 121.7, 121.5, 115.2, 76.5, 30.9, 23.1, 10.2 ppm; MS (EI) *m*/*e* 607 (M^+). Anal. Calcd for $C_{40}H_{49}O_4N$: C, 79.04; H, 8.13; N, 2.30. Found: C, 78.82, H, 8.65, N, 2.33.

5-*N*-Formamyl-25,26,27,28-tetra-*n*-propoxycalix[4]arene (10). A solution containing compound **9** (0.42 g, 0.69 mmol) in formic acid (20 mL) and toluene (100 mL) was refluxed several hours. The excess of formic acid and water was eliminated using a Dean−Stark apparatus, prior to evaporate the solution to dryness. The white solid was purified by column chromatography using CH_2Cl_2: yield 100% (0.44 g); T_m = 171 °C; IR solid ν (cm^{-1}) 1690 (C═O); ^{1}H NMR ($CDCl_3$) 8.156−8.159 (2 s, 1H, CHO), 7.94 (br s, 0.5H, *NH*CHO), 7.91 (br s, 0.5H, *NH*CHO), 6.2−7.05 (m, 9H, Ph), 5.85 (s, 2H, Ph) 4.44 (d, 4H, J = 13.5, CH_2), 3.75−4.01 (m, 4H, OCH_2), 3.70 (t, 4H, J = 7.0, OCH_2), 3.16 (d, 2H, J = 14.0, CH_2), 3.11 (d, 2H, J = 14.0, CH_2), 1.82−1.98 (m, 8H, CH_2CH_3), 0.87−1.11 ppm (m, 12H, CH_3); ^{13}C NMR ($CDCl_3$) 163.1, 158.5, 157.2, 156.6, 155.6, 153.6, 136.4, 135.7, 135.4, 134.8, 133.8, 130.3, 128.9, 128.4, 128.1, 127.8, 127.4, 121.9, 121.5, 120.0, 119.0, 77.0, 76.7, 76.4, 30.8, 23.3, 23.0, 22.9, 10.5, 10.1, 9.8 ppm; MS (EI) *m*/*e* 635 (M^+). Anal. Calcd for $C_{41}H_{49}O_5N$: C, 77.45; H, 7.77; N, 2.20. Found: C, 77.42; H, 8.10; N, 2.26.

5-Isocyano-25,26,27,28-tetra-*n*-propoxycalix[4]arene (11). A solution containing compound **10** (0.16 g, 0.25 mmol) and Et_3N (68 μL, 0.49 mmol) in dry CH_2Cl_2 (10 mL) was refluxed under inert atmosphere. A CH_2Cl_2 solution containing diphosgene (0.15 mL, 1.2 mmol) was added over a period of 10 min. The solution was refluxed for 2 days and cooled to room temperature. The resulting solution was extracted twice with distilled water, and the organic phase was separated and evaporated. The white solid was purified by column chromatography using a CH_2Cl_2/hexanes 40:60 mixture: yield 70% (0.11 g); T_m = 162−164 °C; IR ($CHCl_3$) ν (cm^{-1}) 2126 cm^{-1} (N≡C); ^{1}H NMR ($CDCl_3$) 6.99 (dd, 2H, J = 7.0, J = 1.5, Ph), 6.92 (dd, 2H, J = 7.5, J = 1.5, Ph), 6.84 (t, 2H, J = 7.5, Ph), 6.51 (t, 1H, J = 7.5, Ph), 6.25 (d, 2H, J = 7.5, Ph), 6.20 (s, 2H, Ph), 4.44 (d, 2H, J = 13.5, CH_2), 4.41 (d, 2H, J = 13.5, CH_2), 3.8−4.0 (m, 4H, OCH_2), 3.72 (t, 4H, J = 7.0, OCH_2), 3.17 (d, 2H, J = 13.5, CH_2), 3.09 (d, 2H, J = 13.5, CH_2) 1.80−2.00 (m, 8H, CH_2CH_3), 1.06 (t, 6H, J = 7.5, CH_3), 0.90 ppm (t, 6H, J = 7.5, CH_3); ^{13}C NMR (CD_2Cl_2) 161.8, 157.8, 156.9, 156.2, 137.1, 136.4, 135.7, 134.4, 129.6, 128.8, 127.9, 125.9, 122.4, 122.1, 77.4, 77.2, 77.2, 31.2, 31.1, 23.8, 23.4, 10.8, 10.1 ppm; MS (EI) 617 (M^+). Anal. Calcd for $C_{41}H_{47}O_4N$: C, 79.71; H, 7.67; N, 2.27. Found: C, 79.68; H, 7.80; N, 2.31. UV−vis (EtOH) [λ_{max}/nm (ϵ/M^{-1} cm^{-1})]: 218 sh (104 000), 247 sh (41 500), 265 sh (2400).

Chloro(5-isocyano-25,26,27,28-tetra-*n*-propoxycalix[4]arene)gold-(I) (12). A solution containing compound **11** (20 mg, 32 μmol) in CH_2Cl_2 (10 mL) was added to a CH_2Cl_2 solution (10 mL) containing $Au(SC_4H_8)Cl$ (10 mg, 32 μmol) under inert atmosphere. The solution was stirred for 6 h at room temperature, and the solvent was evaporated. The resulting oil was purified by column chromatography using a CH_2Cl_2/hexanes 50:50 mixture: yield 90% (24 mg); T_m >200 °C (dec); IR ($CHCl_3$) ν (cm^{-1}) 2214 cm^{-1} (N≡C); ^{1}H NMR($CDCl_3$) 7.10 (dd, 2H,

Table 1. Crystallographic Data Collection Parameters for **5**

formula	$C_{44}H_{44}O_4N_4 \cdot C_5H_{12}O$
fw	780.94
space group	$P2_1/c$
a (Å)	14.990(1)
b (Å)	14.463(1)
c (Å)	21.172(1)
α (deg)	90
β (deg)	95.59(1)
γ (deg)	90
V (Å^3)	4568.5(2)
Z	4
ρ_{calcd} (g cm^{-3})	1.185
temp (K)	298(1)
linear abs coeff (mm^{-1})	0.583
cryst size (mm^3)	0.20 × 0.20 × 0.20
radiation	Cu Kα (λ = 1.541 84 Å)
final R indices [I(net) ≥ 2.0σ(I_{net})][a]	0.0843
Final wR indices [I(net) ≥ 2.0σ(I_{net})][a]	0.2358

[a] $R(F) = (\Sigma_i||F_{obs}|_i - |F_{calc}|_i|)/(\Sigma_i|F_{obs}|_i|)$. $wR(F) = [(\Sigma_i\{w_i(F_{obs}^2{}_I - F_{calc}^2{}_i)\}^2)/(\Sigma_i\{w_i(F_{obs}^2{}_i)\}^2)]^{1/2}$.

J = 7.5, J = 1.5, Ph), 7.00 (dd, 2H, J = 7.5, J = 1.5, Ph), 6.93 (t, 2H, J = 7.5, Ph), 6.39 (t, 1H, J = 7.5, Ph), 6.17−6.20 (m, 3H, Ph), 4.45 (d, 2H, J = 14.0, CH_2), 4.43 (d, 2H, J = 13.5, CH_2), 3.84−4.03 (m, 4H), 3.74 (t, 2H, J = 7.0, OCH_2), 3.70 (t, 2H, J = 7.0), 3.19 (d, 2H, J = 13.5, CH_2), 3.13 (d, 2H, J = 14.0, CH_2), 1.80−1.95 (m, 8H, CH_2-CH_3), 0.89 ppm (t, 12H, J = 7.5, CH_3); ^{13}C NMR ($CDCl_3$) 158.3, 157.6, 155.6, 137.2, 136.2, 135.2, 133.7, 129.8, 128.5, 127.4, 125.9, 122.5, 121.6, 117.9, 77.3, 77.0, 31.0, 23.5, 23.0, 10.7, 10.6, 9.9 ppm; MS (EI) m/e 849 (M^+). Anal. Calcd for $C_{41}H_{47}O_4NClAu$: C, 57.92; H, 5.57; N, 1.65. Found: C, 57.87; H, 5.51; N, 1.68. UV−vis (EtOH) [λ_{max}/nm (ϵ/M^{-1} cm^{-1})]: 280 nm (2500).

Crystallography. Single crystals suitable for crystal structure analysis were obtained from vapor diffusion of *t*-BuOMe into a solution of **5** in CH_2Cl_2. Intensity data were collected at 293(1) K, on an Enraf-Norrius CAD-4 automatic diffractometer. Table 1 provides the crystallographic and data collection details. Cell constants and an orientation matrix for data collection were obtained from a least-squares refinement using the setting angles of 24 centered reflections in the range 40° ≤ 2θ ≤ 50°. Space group determination was based upon systematic absences, packing considerations, a statistical analysis of intensity distribution, and the successful solution and refinement of the structure. The NRCCAD program[18] was used for centering, indexing, and data collection. Two standard reflections were measured every 60 min. The NRCVAX programs[19] were used for crystal structure solution by application of direct methods. The SHELX-97 program[20] was used for refinement by full-matrix least squares on F^2. ψ scan based empirical absorption corrections were made; the maximum and minimum transmission factors are given in Table 1. No significant decay was observed during data collection. Isotropic extinction coefficients were included in the refinement to account for secondary extinction effects.[21] Hydrogen atoms were all geometrically placed, and the respective final refinements included anisotropic thermal parameters for the non-hydrogen atoms and isotropic thermal parameters for the hydrogen atoms. Individual displacement parameters were fixed at $U(H) = 1.5U_{eq}$(C-methyl) or $U(H) = 1.2U_{eq}(C)$ and were treated as riding for refinement. The $R(F)$ and $R_w(F^2)$ final discrepancy indices at convergence for the $I_{net} \geq 2.0\theta(I_{net})$ significant reflections, the number of restraints and variables, and the GoF are listed in Table 1. Two of the four isopropyl groups are disordered. Those were refined using several restraints (option SAME in SHELXL-97) to avoid unrealistic geometries. One molecule of solvent is found in the asymmetric unit.

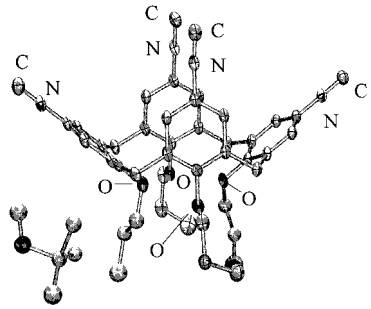
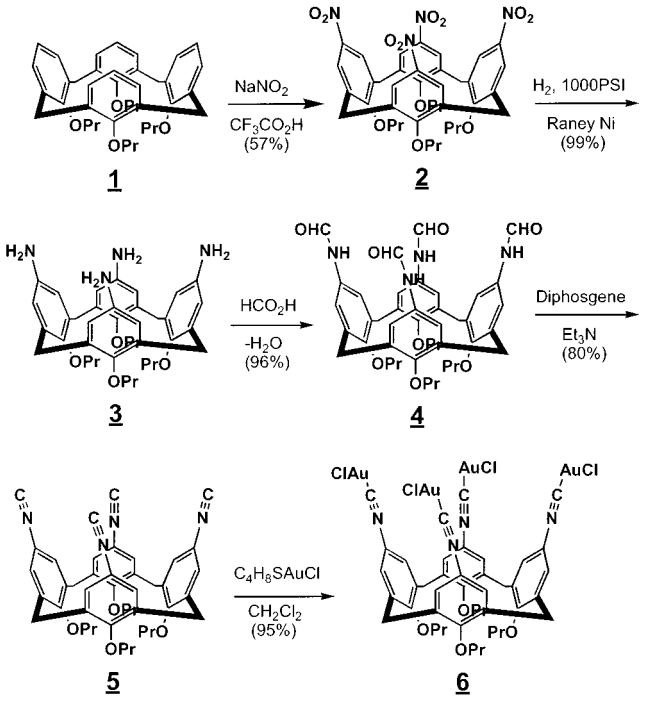


Figure 1. ORTEP drawing of **5**·*t*-BuOMe. The ellipsoids are shown at 30% probability, and the H atoms are not shown for clarity.

Scheme 1



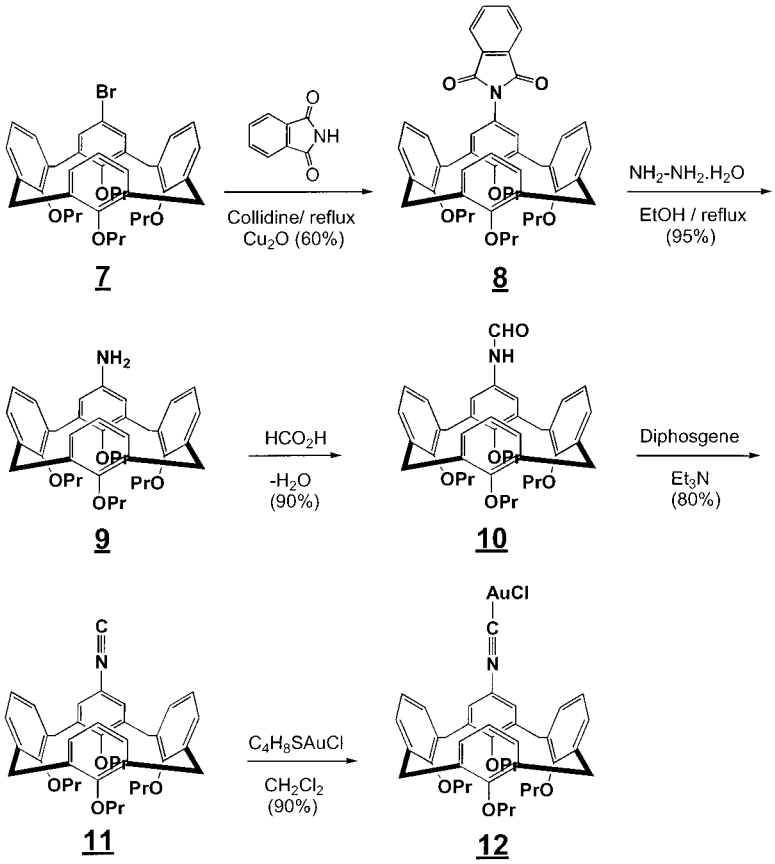
Apparatus. The 298 K UV−vis spectra were recorded on a model 8452A HP spectrometer. The luminescence spectra were measured on a double monochromator Fluorolog 1902 instrument from SPEX, using a 400 W Hg−Xe high-pressure lamp. Emission lifetimes were acquired on a PTI LS-100 spectrometer using Xe-pulsed lamp. The pulse width of ∼1 μs determinated the lower limit of the measurements. The solutions were degassed using argon gas.

Results and Discussion

The preparation **6** is performed in five steps from **1** with an overall yield of 40% (Scheme 1). The introduction of four N-containing groups onto the upper rim proceeds using sodium nitrite in trifluoroacetic acid, to form the tetranitrated compound **2**.[22] The subsequent catalytic hydrogenation of the nitro groups is effected quantitatively under Raney Ni and hydrogen, to afford the tetraamine derivative **3**.[23] The conversion of the amine residues into isocyanides is performed using the dehydration method of formamides by diphosgene.[24] Indeed, the tetrafor-

(18) Le Page, Y.; White, P. S.; Gabe, E. J. NRCCAD. An Enhanced CAD-4 Control Program. *Proc. Am. Crystallogr. Hamilton Meet.* **1986**, Abstract PA23.
(19) Gabe, E. J.; Le Page, Y.; Charland, J. P.; Lee, F. L.; White, P. S. *J. Appl. Crystallogr.* **1989**, *22*, 384.
(20) Sheldrick, G. M. *SHELXL97 Programs for Crystal Structure Analysis (Release 97-2)* Sheldrick, G. M.; Institut fur Anorganische Chemie der Universitat: Tammanstrasse 4, D-3400, Gottingen, Germany, 1998.
(21) Larson, A. C. *Crystallographic Computing*; FRA, Eds.; Munksgaard: Copenhagen, 1970; p 291.
(22) (a) This compound can also be prepared according to a literature procedure outlined in ref 22b using nitric acid and 5,11,17,23-tetra-*p*-*tert*-butyl-25,26,27,28-tetrapropoxycalix[4]arene but in lower yields in these experiments. (b) Parker, D. *Macrocycle Synthesis, A Practical Approach*; Oxford University Press: Oxford, U.K., 1996; p 170.

Scheme 2



mamided product **4** is obtained in good yields via condensation of formic acid with the amine residues. Conveniently the low solubility of **4** in common organic media such as halogenated solvents, acetone, and toluene (here as reaction solvent) provokes its precipitation, which eases its purification. The ^{1}H NMR spectral analysis for **4** in deuterated DMSO reveals absence of the expected C_{4v}, C_{2v}, or C_s symmetry. This complexity is due to the presence of many isomers issued from the relative orientations of the formamide groups, which must keep coplanarity with the benzene rings to satisfy resonance structures. Despite the low solubility, the dehydratation of **4** is conveniently performed in reasonable to good yields with diphosgene, to generate the ligand **5**. A strong IR absorption is evident at 2130 cm^{-1} for **5,** and characterization by X-ray crystallography (Figure 1) reveals the expected cone conformation of the macrocycle. If the propyl groups are ignored, the local symmetry is C_{2v}, where the face-to-face benzene interplanar angles are $-22.75(5)°$ (inward) and $77.12(9)°$ (outward). The N···N and C···C separations for the corresponding cofacial isocyanides are 3.785(5) and 3.461(5) Å and 12.177(5) and 13.996(5) Å, respectively.

The synthesis of **6** proceeds with the addition of a stoichiometric amount of chloro(tetrahydrothiophene)gold(I), to produce an insoluble white material which analyzes as [Pr_4calix[4]arene-$(NC)_4$]Au_4Cl_4·0.25C_4H_8S. The presence of the ν(NC) band at 2121 cm^{-1} confirms the complexation, and the resonances of the aromatic protons at the ortho-positions of the isocyanide groups undergo a 0.38 ppm shift with respect with the free ligand **5**. ^{1}H NMR spectra in the methylene region (two doublets) indicate that the cone conformation is retained in **6**. The mass spectra (MALDI-TOF) exhibit a strong peak at ~1584 amu (100% relative intensity) with many isotopic components, which corresponds to the [Pr_4calix[4]arene$(NC)_4$]Au_4Cl_3 fragment. The reduced solubility prevented a crystal of suitable quality from being obtained.

The syntheses of the monodentate ligand **11**, and its corresponding gold(I) chloride complex **12**, are shown in Scheme 2. Using **7** as starting material, incorporation of an N-atom is achieved with phthalimide (Gabriel's reaction), to form **8**. The latter is converted in good yield into the monoamine compound **9**, using hydrazine as deproctecting agent. The synthesis of the isocyanide derivative **11** is performed in two steps from the formation of the formamide molecule **10**, followed by its dehydratation with diphosgene. The new ligand exhibits a peak at 617 amu in the EI mass spectra, corresponding to the molecular ion, and ν(NC) is found at 2126 cm^{-1}. The subsequent complexation with chloro(tetrahydrothiophene)gold(I) leads to **12**, which shows a peak at 849 amu (EI; molecular ion) and a strong IR absorption at 2214 cm^{-1}.

The free ligands **5** and **11**, and corresponding gold(I) complexes **6** and **12,** exhibit quasi-identical UV−vis spectra, with a shoulder at 280 nm ($\epsilon \sim 2500$ M^{-1} cm^{-1}) that is unambiguously assigned to a phenyl-localized $\pi-\pi^*$ absorption.[25] The ligands are not luminescent at 298 K both in solutions and in the solid state, but **6** and **12** are (Figures 2 and 3). In EtOH solutions, weak and asymmetric emission bands are seen at 450 nm ($\tau_e < 1$ μs), while in the solid state stronger emissions are detected. The emission lifetimes are 3.1 ± 0.1 and 17.2 ±

(23) This method is found far more satisfactory than that of palladium in activated carbon as catalyst, even for prolonged reaction times (up to 72 h), as incomplete reactions are observed.

(24) (a) The diphosgene methodology[24b] is favored over the carbene chemistry ($CHCl_3$ and NaOH),[24c] due to the significantly lower yields generally obtained with the latter. (b) March, J. *Advanced Organic Chemistry*, 4th ed.; Wiley: New York, 1992; p 417. (c) Weber, W. P.; Gokel, G. W.; Ugi, I. K. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 530.

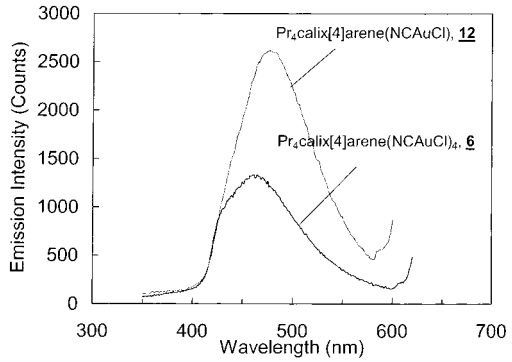


Figure 2. Solid-state emission of **6** and **12** at 298 K. $\lambda_{exc} = 310$ nm. Slit widths: 500 μm for both excitation and emission.

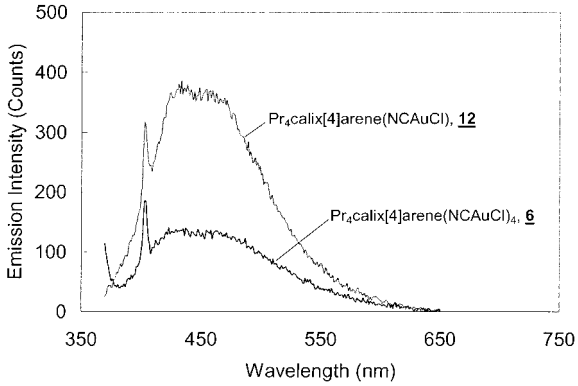


Figure 3. Emission spectra of **6** and **12** in degassed EtOH at 298 K. $\lambda_{exc} = 310$ nm. Slit widths: 500 μm for both excitation and emission. The spikes at 405 nm are due to scatterings.

0.2 μs ($\lambda_{max} = 460$ nm) for **6** and **12**, respectively, and reflect the anticipated greater heavy atom effects for **6**. On the basis of these relatively long τ_e's and the large Stoke shifts between absorption and emission (>15 000 cm^{-1}), these luminescences are assigned to $\pi-\pi^*$ phosphorescence.[25] Absence of shift in the emission bands between **6** and **12** in solutions indicates that no, or very weak, intramolecular Au···Au interactions occur.

These results contrast those reported for $Au_2(dcpm)_2^{2+}$ (dppm = $Cy_2PCH_2PCy_2$; intramolecular Au_2 distance ~3 Å), where a strong dσ^*-pσ absorption at 280 nm and a spin-forbidden dσ^*-pσ^* emission at 370 nm are seen.[26] Similarly, recent work on an acetyl complex $[Au(C{\equiv}CPh)]_2(dppe)$ (dppe = $Ph_2PCH_2CH_2PPh_2$) demonstrated that no Au···Au interaction occurs in solutions, where a strongly structured emission assigned to MLCT (L = C≡CPh) was found at 450 nm.[27]

The absence of Au···Au interactions in **6** may be explained by steric Cl···Cl contacts for the face-to-face tilting of the isocyanobenzene fragments toward each other. The sum of the van der Waals radii (3.6 Å)[28] puts the Au···Au distance in the long range for such interactions.[29]

The mono- and tetrafunctionalization of the calix[4]arene upper rim by isocyanide groups is easily achieved.[30] These new assembling ligands permit the construction of metallic architectures which may lead to larger cavities and to M_2 proximity and cooperations. These ligands do not, however, favor strong M_2 interactions, if any. Mixed donor atom and chiral assembling calix[4]arenes can be synthesized using adequate protecting groups and appropriate preparation methodologies, affording versatile multidentate ligands. Hence, mixed-metal complexes of functionalized calix[4]arene in the upper rim can be prepared.

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Supporting Information Available: Listings giving crystal data, atomic coordinates, bond lengths and angles, anisotropic displacement parameters, hydrogen coordinates, torsion angles, and least-squares planes in tabular and CIF format, an atom numbering diagram for **5**, an MO analysis and diagram for PhNCAuCl, and text detailing the synthesis of **14**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(25) These assignments are supported by EHMO computations which predict that the frontier MOs are intraligand-localized (PhNC) π and π^* orbitals with practically no Au contributions. The data are available in the Supporting Information. The localized Au orbitals are greatly stablilized, and a lowest energy MLCT transition is very unlikely, as clearly seen in the UV−vis spectra.

(26) Fu, W.-F.; Chan, K. C.; Miskowski, V. M.; Che, C.-M. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 2783.
(27) Li, D.; Hong, X.; Che, C.-M.; Lo, W.-C.; Peng, S.-M. *J. Chem. Soc., Dalton Trans.* **1993**, 2929.
(28) Cotton, F. A.; Wilkinson, G.; Gaus, P. L. *Basic Inorganic Chemistry*, 3rd ed.; John Wiley: New York, 1995; p 61.
(29) Computer modelings (PC model) predict that the tilted cofacial Cl···N axes are not parrallel, but slightly cross, decreasing the Au···Au distance. No close Au···Au contact is found.
(30) The 5,17-derivatization can also be acheived from 25,27-dibenzoylcalix[4]arene.[11] The benzoyl groups render the benzene ring electron poor. Hence, nitration reactions occur faster on the phenol residues and lead to clean incorporation of two N atoms on the upper rim of the calix[4]arene bowl (Supporting Information).