Supporting Information

Cationic Recognition by *t*-Butylcalix[4]arene-Functionalized Nanoprobes

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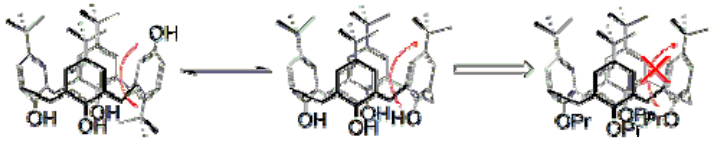
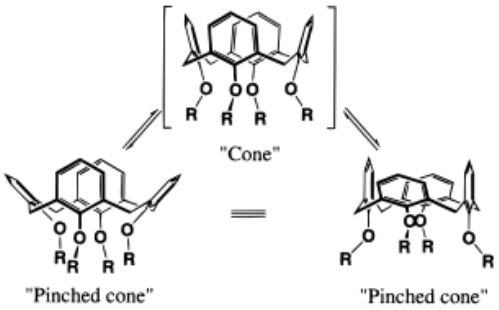
0. Molecular structure of calixarene



(A)



(B)

Scheme S1. (A) The modes for inversion of the phenyl unit; (B) C_{2v} -C_{2v} interconversion of tetra-alkoxycalix[4]arene in the cone conformer. (ref. Atsushi Ikeda, Seiji Shinkai. "Novel Cavity Design Using Calix[n]arene Skeletons: Toward Molecular Recognition and Metal Binding". *Chem. Rev.* **1997**, *97*, 1713−1734)

1. Details of the Ligand Synthesis

*(1) Synthesis of the **9**, **10**.* 1, 4-dibromobutane (0.55 mL, 4.5mmol) was diseolved in acetone (20 mL**),** and the solution was heated in the presence of K_2CO_3 (6.2 g, 45mmol) at 50 ^oC for 30 min. Then, to the above suspension was added a solution of 4-iodophenol (1.0 g, 4.5mmol) in acetone (10 mL) over a period of 4 h by a machine. The reaction mixture was cooled to room temperature and filtered. The filtrate was evaporated in vacuo, and the residue was chromatographed (SiO_2; eluent, Hexane/ CH_2Cl_2, 10: 1) to give 0.91 g of **9** (57%) and 0.28 g of **10** (12.5%),

respectively. **9**: ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 1.93 (m, 2H, CH_2), 2.04 (m, 2H, CH_2), 3.48 (t, J = 6.8 Hz, 2H, CH_2), 3.95 (t, J = 6.4 Hz, 2H, CH_2), 6.66 (d, J = 8.8 Hz, 2H, ArH), 7.55 (d, J = 8.4 Hz, 2H, ArH); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 27.73 (CH_2), 29.34 (CH_2), 33.36 (CH_2), 66.90 (CH_2), 82.72 (C), 116.82 (CH), 138.18 (CH), 158.68 (C). **10**: ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 1.95 (t, 4H, CH_2), 3.98 (t, 4H, CH_2), 6.66 (d, 2H, ArH), 7.55 (d, 2H, ArH); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 25.81 (CH_2), 67.44 (CH_2), 82.63 (C≡), 116.83 (CH_2), 138.17 (CH_2), 158.75 (C).

(2) Synthesis of the **5**. *t*-BCA **4** (2.89 g, 4.45 mmol), *n*-BuBr (12 mL, 132 mmol) were diseolved in DMF (20 mL**),** and the solution was heated in the presence of $Ba(OH)_2{\cdot}8H_2O$ (4.2 g, 13.75 mmol) and BaO (3.95 g, 25.8 mmol) at 30 °C for 3 h. After evaporation of the solvent the mixture was taken up in CH_2Cl_2, (100 mL) and washed with NH_4Cl (2 × 25 mL) and brine (2 × 25 mL). The organic layer was dried with $MgSO_4$, and filtered. The solvent was evaporated in vacuo, and the residue was chromatographed (SiO_2; eluent, Hexane/CH_2Cl_2, 3: 1) to give 3.22 g of **5** (89%) as a white solid. m.p. 136~138 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.82 (s, 18H, CH_3), 0.99 (t, J = 7.6 Hz, 6H, CH_3), 1.04 (t, J = 7.2 Hz, 3H, CH_3), 1.32 (s, 18H, CH_3), 1.40 (m, 2H, CH_2), 1.56 (m, 4H, CH_2), 1.83 (m, 2H, CH_2), 1.95 (m, 2H, CH_2), 2.29 (m, 2H, CH_2), 3.20 (m, 4H, $ArCH_2Ar$), 3.79 (m, 4H, CH_2), 3.90 (t, J = 8.4 Hz, 2H, CH_2), 4.35 (m, 4H, $ArCH_2Ar$), 5.67 (s, 1H, –OH), 6.51 (m, 4H, ArH), 7.04 (s, 2H, ArH), 7.13 (s, 2H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 14.06 (CH_3), 19.58 (CH_3), 31.04 (CH_3), 31.09 (CH_2), 31.27 (CH_2), 31.67 (CH_3), 31.74 (CH_3), 32.40 (CH_2), 33.62 (C), 33.81 (C), 34.10 (C), 74.67 (CH_2), 76.00 (CH_2), 124.62 (CH), 124.70 (CH), 124.94 (CH), 125.55 (CH), 129.36 (C), 131.86 (C), 132.23 (C), 135.99 (C), 141.30 (C), 144.96 (C), 145.42 (C), 150.65 (C), 151.74 (C), 153.98 (C); APCI–MS m/z: 1197.0 (M^+, 100).

(3) Synthesis of the ***6.*** *t*–BCA **5** (1.8 g, 2.35 mmol) was treated with oil-dispersed NaH (560 mg, 23.2 mmol) in DMF (20 mL) for 1.5 hr at 50 °C, and then **9** (1.0 g, 2.82 mmol) which was dissolved in DMF was added. The reaction mixture was refluxed for 20 h. Excess NaH was decomposed with methanol. The mixture was diluted with water (200 mL) and extracted with CH_2Cl_2 (3 × 20 mL). The organic layer was washed with NH_4Cl (2 × 25 mL) and brine (2 × 25 mL), dried with $MgSO_4$, and filtered. The solvent was evaporated in vacuo, and the residue was chromatographed (SiO_2; eluent, Hexane/CH_2Cl_2, 3: 1) to give 0.66 g of **6** (88%) as a white solid. m.p. 106~108 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.98 (t, J = 7.6 Hz, 9H, CH_3), 1.06 (s, 18H, CH_3), 1.09 (s, 18H, CH_3), 1.43 (m, 6H, CH_2), 1.93 (m, 2H, CH_2), 2.00 (m, 6H, CH_2), 2.18 (m, 2H, CH_2), 3.12 (m, 4H, $ArCH_2Ar$), 3.84 (m, 6H, CH_2), 3.94 (t, J = 7.6 Hz, 2H, CH_2), 4.00 (t, J = 6.4 Hz, 2H, CH_2), 4.40 (d, J = 8.4 Hz, 4H, $ArCH_2Ar$), 6.69 (d, J = 8.8 Hz, 2H, ArH), 6.75 (s, 4H, ArH), 6.80 (s, 4H, ArH), 7.55 (d, J = 8.8 Hz, 2H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 14.20 (CH_3), 14.26 (CH_3), 19.35 (CH_3), 19.40 (CH_3), 25.99 (CH_2), 26.83 (CH_2), 31.07 (CH_2), 31.43 (CH_3), 31.47 (CH_3), 32.38 (CH_2), 33.78 (C), 33.81 (C), 68.03 (CH_2), 74.70 (CH_2), 75.11 (CH_2), 75.15 (CH_2), 82.49 (C), 116.84(CH), 124.79 (CH), 124.89 (CH), 124.97 (CH), 133.58 (C), 133.73 (C), 133.92 (C), 138.15 (CH), 144.18 (C), 144.38 (C), 153.61 (C), 153.75 (C), 158.95 (C).

(4) Synthesis of the ***7***. A suspension of *t*-BCA **4** (0.4 g, 0.62 mmol), K_2CO_3 (0.33 g, 2.39 mmol), and **9** (0.53 g, 1.49 mmol) in CH_3CN (40 mL) was refluxed for 16 h. After evaporation of the solvent the mixture was taken up in CH_2C1_2, (100 mL) and washed with NH_4Cl (2 × 25 mL) and brine (2 × 25 mL). The organic layer was dried with $MgSO_4$, and filtered. The solvent was evaporated in vacuo, and the residue was chromatographed (SiO_2; eluent, Hexane/CH_2Cl_2, 3: 1) to give 0.57 g of **7** (71%) as a white solid. m.p. 182~184 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ:

0.99 (s, 18H, CH_3), 1.29 (s, 18H, CH_3), 2.18 (m, 8H, CH_2), 3.32 (d, J = 13.2 Hz, 4H, $ArCH_2Ar$), 4.01 (m, 8H, CH_2), 4.27 (d, J = 13.2 Hz, 4H, $ArCH_2Ar$), 6.63 (d, J = 8.8 Hz, 4H, ArH), 6.84 (s, 4H, ArH), 7.06 (s, 4H, ArH), 7.49 (d, J = 8.8 Hz, 4H, ArH), 7.69 (s, 2H, –OH); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 25.97 (CH_2), 26.76 (CH_2), 31.01 (CH_3), 31.77 (CH_3), 33.80 (C), 33.94 (C), 67.61 (CH_2), 75.82 (CH_2), 82.60 (C), 116.85 (CH), 125.09 (CH), 125.50 (CH), 127.64 (C), 132.59 (C), 138.16 (CH), 141.48 (C), 146.89 (C), 149.74 (C), 150.66 (C), 158.80 (C); APCI–MS *m/z*: 1197.0 (M^+, 100).

*(5) Synthesis of the **8**.* *t*-BCA **4** (320 mg, 0.49 mmol) was treated with oil-dispersed NaH (95 mg, 3.96 mmol) in DMF (20 mL) for 0.5 hr at r.t., and then **9** (1.04 g, 2.94 mmol) which was dissolved in DMF was added. The reaction mixture was stirred at 50 ^{o}C for 20 h. Excess NaH was decomposed with methanol. The mixture was diluted with water (200 mL) and extracted with CH_2Cl_2 (3 × 20 mL). The organic layer was washed with NH_4Cl (2 × 25 mL) and brine (2 × 25 mL), dried with $MgSO_4$, and filtered. The solvent was evaporated in vacuo, and the residue was chromatographed (SiO_2; eluent, Hexane/CH_2Cl_2, 5: 1) to give 0.73 g of **8** (85%) as a white solid. m.p. 192~195 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.08 (s, 36H, CH_3), 1.85 (m, 8H, CH_2), 2.14 (m, 8H, CH_2), 3.14 (d, J = 12.4 Hz, 4H, $ArCH_2Ar$), 3.86 (t, J = 6.4 Hz, 8H, CH_2), 3.93 (t, J = 8.0 Hz, 8H, CH_2), 4.38 (d, J = 12.4 Hz, 4H, $ArCH_2Ar$), 6.55 (d, J = 8.4 Hz, 8H, ArH), 6.79 (s, 8H, ArH), 7.46 (d, J = 8.8 Hz, 8H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 26.06 (CH_2), 26.96 (CH_2), 31.09 (C), 31.43 (CH_3), 33.82 (CH_2), 67.86 (CH_2), 74.80 (CH_2), 82.68 (C), 116.69 (CH), 125.01 (CH), 133.63 (C), 138.21 (CH), 144.56 (C), 153.35 (C), 158.72 (C); APCI–MS *m/z*: 1745.7 (M^+, 100).

*(6) Synthesis of the **1**.* A 100 mL two-necked flask was charged with **6** (663 mg, 0.61 mmol), $(Ph_3P)_2PdCl_2$ (85 mg, 0.12 mmol), CuI (23 mg, 0.12 mmol), diisopropylamine (5 mL), and toluene (20 mL) under nitrogen. Then, to the above suspension was added a solution of **11** (127 mg, 0.85 mmol) in toluene (20 mL) over a period of 10 h at 65 °C by a machine. The reaction mixture was cooled to room temperature and filtered. The filtrate was poured into aqueous NH_4Cl, and extracted with CH_2Cl_2 (3 × 20 mL). The extract was then washed with brine, dried over $MgSO_4$, and filtered. The solvent was evaporated in vacuo, and the residue was chromatographed (SiO_2; eluent, Hexane/CH_2Cl_2, 3: 1) to give 224 mg of **1** (33%) as a yellow solid. m.p. 108~110 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.97 (m, 9H, CH_3), 1.07 (s, 18H, CH_3), 1.10 (s, 18H, CH_3), 1.44 (m, 6H, CH_2), 1.98 (m, 8H, CH_2), 2.20 (m, 2H, CH_2), 2.49 (s, 3H, SCH_3), 3.12 (m, 4H, $ArCH_2Ar$), 3.85 (m, 6H, CH_2), 3.96 (t, J = 7.6 Hz, 2H, CH_2), 4.06 (t, J = 6.0 Hz, 2H, CH_2), 4.41 (d, J = 12.4 Hz, 4H, $ArCH_2Ar$), 6.76 (s, 4H, ArH), 6.81 (s, 4H, ArH), 6.88 (d, J = 7.2 Hz, 2H, ArH), 7.20 (d, J = 8.0 Hz, 2H, ArH), 7.42 (d, J = 7.2 Hz, 2H, ArH), 7.45 (d, J = 7.2 Hz, 2H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 14.18 (CH_3), 14.23 (CH_3), 15.48 (SCH_3), 19.38(CH_2), 19.42(CH_2), 26.08 (CH_2), 26.88 (CH_2), 31.07 (CH_2), 31.11 (CH_2), 31.44 (CH_3), 31.48 (CH_3), 32.41 (CH_2), 33.78 (C), 33.82 (C), 68.02 (CH_2), 74.72 (CH_2), 75.10 (CH_2), 75.15 (CH_2), 87.78 (C≡), 89.56 (C≡), 114.49 (CH), 115.25 (C), 120.03 (C), 124.82 (CH), 124.91 (CH), 124.99 (CH), 125.98 (CH), 131.71 (CH), 132.97 (CH), 133.59 (C), 133.73 (C), 133.93 (C), 133.96 (C), 138.76 (C), 144.18 (CH), 144.21 (C), 144.39 (C), 153.62 (C), 153.79 (C), 159.15 (C); APCI–MS *m/z*: 1128.5 (M^++H_2O, 100); IR (KBr) ν: 3054, 2987, 2930, 2306 (C≡C), 1635, 1422, 1265, 896, 744, 705 cm^{-1}.

*(7) Synthesis of the **2**.* A 100 mL two-necked flask was charged with **7** (255 mg, 0.19 mmol), $(Ph_3P)_2PdCl_2$ (50 mg, 0.07 mmol), CuI (8 mg, 0.04 mmol), diisopropylamine (5 mL), and toluene (20 mL) under nitrogen. Then, to

the above suspension was added a solution of **11** (126 mg, 0.85 mmol) in toluene (20 mL) over a period of 10 h at 65 °C by a machine. The reaction mixture was cooled to room temperature and filtered. The filtrate was poured into aqueous NH_4Cl, and extracted with CH_2Cl_2 (3 × 20 mL). The extract was then washed with brine, dried over $MgSO_4$, and filtered. The solvent was evaporated in vacuo, and the residue was chromatographed (SiO_2; eluent, Hexane/EtOH, 3: 1) to give 200 mg of **2** (77%) as a yellow solid. m.p. 244~245 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.99 (s, 18H, CH_3), 1.29 (s, 18H, CH_3), 2.19 (m, 8H, CH_2), 2.48 (s, 6H, SCH_3), 3.33 (d, J = 12.8 Hz, 4H, $ArCH_2Ar$), 4.05 (s, 8H, CH_2), 4.29 (d, J = 12.8 Hz, 4H, $ArCH_2Ar$), 6.81 (d, J = 8.8 Hz, 4H, ArH), 6.83 (s, 4H, ArH), 7.06 (s, 4H, ArH), 7.15 (d, J = 8.4 Hz, 4H, ArH), 7.39 (d, J = 8.0 Hz, 4H, ArH), 7.41 (d, J = 7.6 Hz, 4H, ArH), 7.68 (s, *2*H, –OH); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 15.40 (SCH_3), 26.14 (CH_2), 26.83 (CH_2), 31.03 (CH_3), 31.69 (CH_2), 31.78 (CH_3), 33.81 (C), 33.95 (C), 67.62 (CH_2), 75.93 (CH_2), 87.79 (C≡), 89.57 (C≡), 114.50 (CH), 115.24 (C), 119 (C), 125.09 (CH), 125.51 (CH), 125.85 (CH), 127.69 (C), 131.73 (CH), 132.62 (C), 133.02 (CH), 138.66 (C), 141.46 (C); APCI–MS *m/z*: 1237.2 (M^+, 100); IR (KBr) v: 3054, 2987, 2306 (C≡C), 1624, 1422, 1265, 1121, 896, 742, 705 cm^{-1}.

*(8) Synthesis of the **3***. A 100 mL two-necked flask was charged with **8** (727 mg, 0.42 mmol), $(Ph_3P)_2PdCl_2$ (65 mg, 0.09 mmol), CuI (18 mg, 0.09 mmol), diisopropylamine (5 mL), and toluene (20 mL) under nitrogen. Then, to the above suspension was added a solution of **11** (377 mg, 2.54 mmol) in toluene (20 mL) over a period of 10 h at 65 °C by a machine. The reaction mixture was cooled to room temperature and filtered. The filtrate was poured into aqueous NH_4Cl, and extracted with CH_2Cl_2 (3 × 20 mL). The extract was then washed with brine, dried over $MgSO_4$, and filtered. The solvent was evaporated in vacuo, and the residue was chromatographed (SiO_2; eluent, Hexane/CH_2Cl_2, 2: 1) to give 213 mg of **3** (28%) as a yellow solid. m.p. 268–270 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.09 (s, 36H, CH_3), 1.89 (m, 8H, CH_2), 2.19 (m, 8H, CH_2), 2.45 (s, 12H, SCH_3), 3.16 (d, J = 12.8 Hz, 4H, $ArCH_2Ar$), 3.94 (m, 16H, CH_2), 4.42 (d, J = 12.4 Hz, 4H, $ArCH_2Ar$), 6.75 (d, J = 9.2 Hz, 8H, ArH), 6.80 (s, 8H, ArH), 7.11 (d, J = 8.8 Hz, 8H, ArH), 7.36 (dd, J = 1.6 Hz&8.8 Hz, 16H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 15.38 (SCH_3), 26.23 (CH_2), 27.06 (CH_2), 31.18 (CH_2), 31.46 (CH_3), 33.85 (C), 67.90 (CH_2), 74.94 (CH_2), 87.92 (C≡), 89.53 (C≡), 114.42 (CH), 125.05 (CH), 125.86 (CH), 131.78 (CH), 132.21 (C), 133.09 (CH), 133.69 (C), 138.69 (C), 144.57 (C), 153.48 (C), 158.95 (C); IR (KBr) v: 3054, 2987, 2540, 2342 (C≡C), 1593, 1421, 1265, 1121, 895, 738, 705 cm^{-1}.

2. Additional Optical and Spectroscopic Data

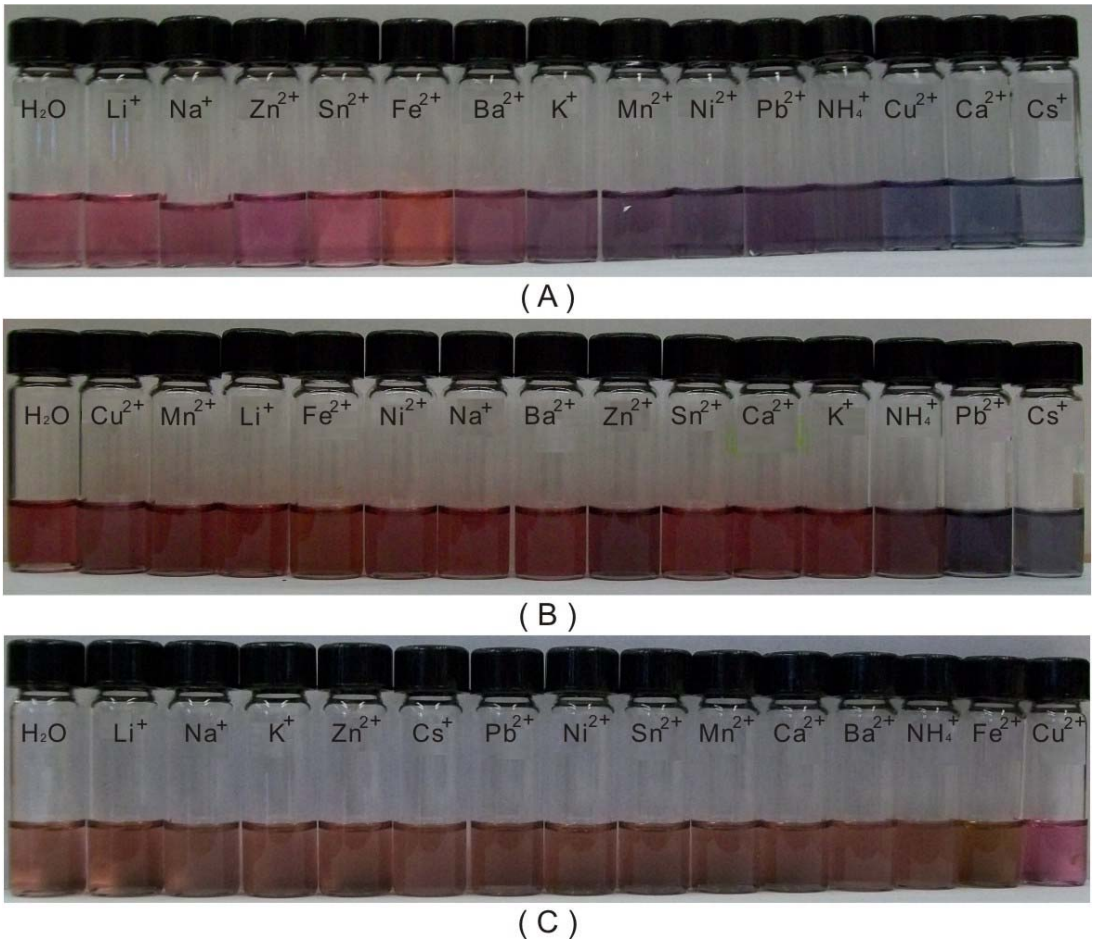


Figure S1. Photos showing the color changes for the methylthio-*t*-BCAmolecules capped gold nanoparticles in response to the addition of different ions ($M^{(n+)}Cl^{-}_{n}$). (A) Au@**1**; (B) Au@**2**; (C) Au@**3**.

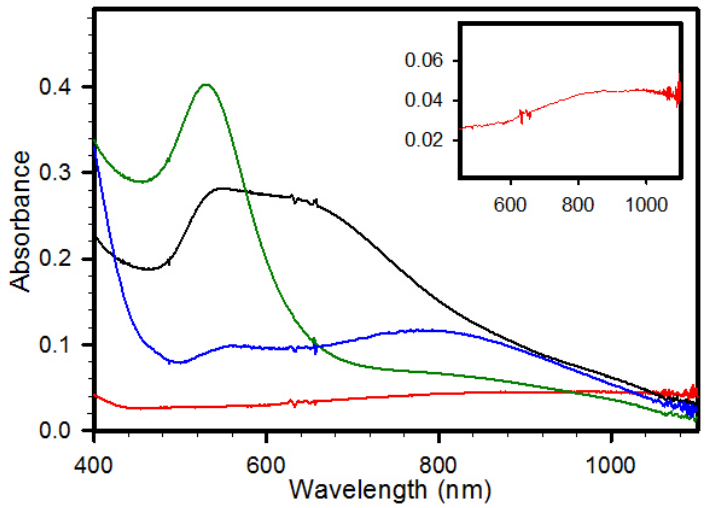
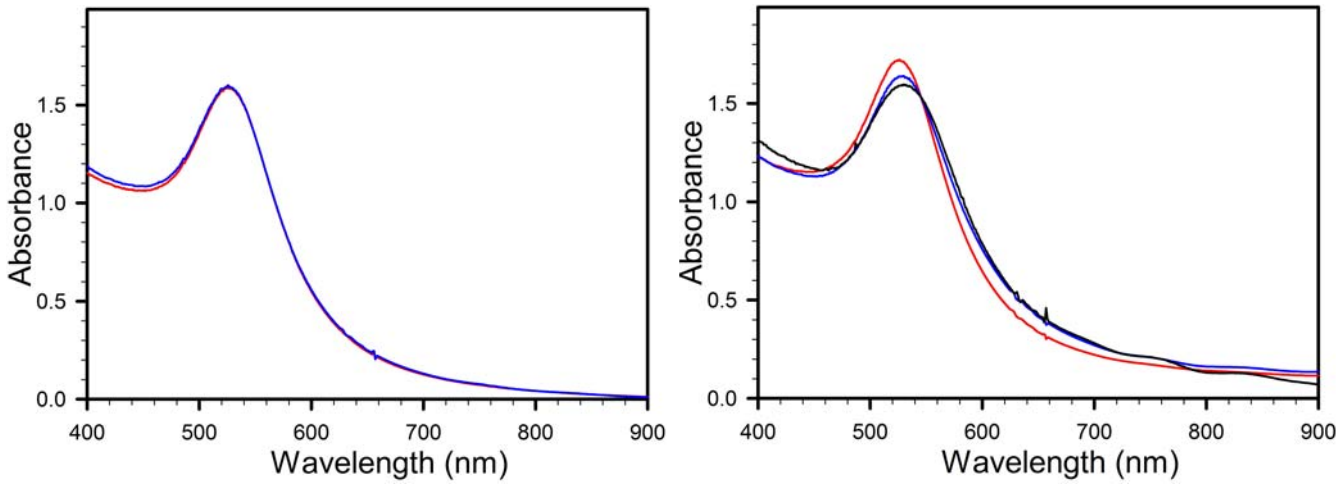
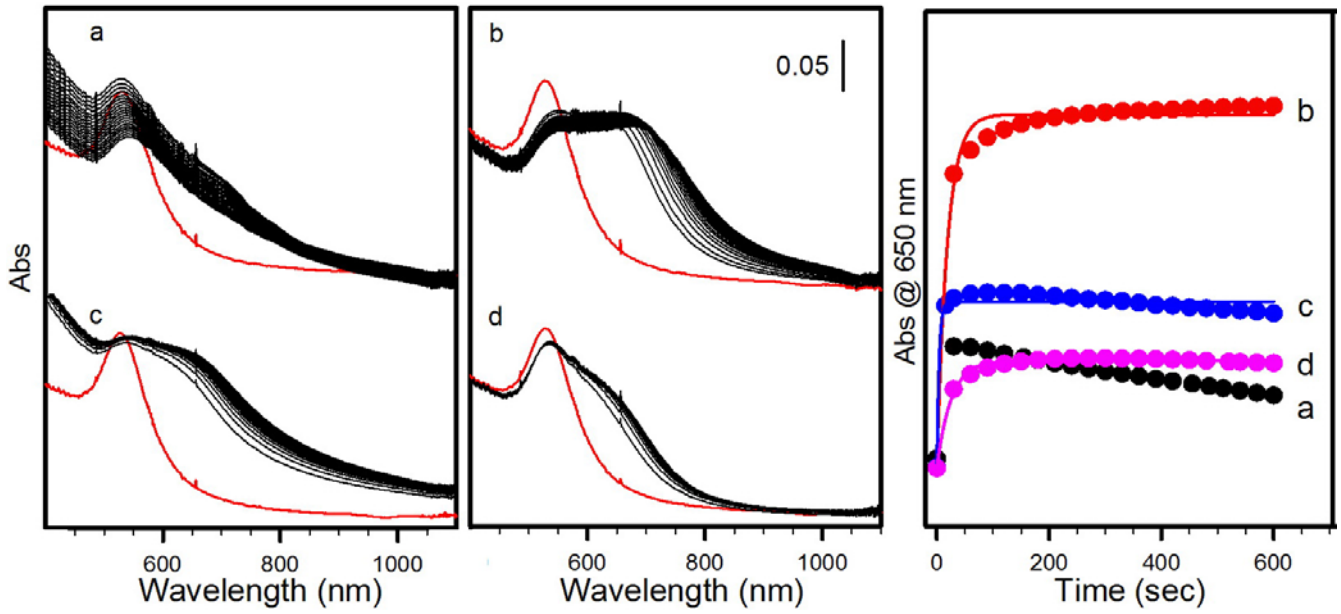


Figure S2. UV-visible spectra obtained from solutions of different methylthio-*t*-butylcalix[4]arenes capped gold nanoparticles in response to Cu^{2+} (1.5 mM). (THF+Cu^{2+} (red); Au@**1**+Cu^{2+} (black); Au@**2**+Cu^{2+} (green); Au@**3**+Cu^{2+} (blue). The insert shows the magnified view of SP band of a pure THF solvent upon addition of Cu^{2+}. This is a control experiment showing pure THF solvent upon addition of Cu^{2+} where a weak peak at 850 nm, corresponding to the absorption band of Cu^{2+}.



(A) (B)

Figure S3. (A) UV-Visible spectra obtained from solutions of Au@**1** (1.75 μM) responding to Na^+ ($[Na^{2+}]/[Au@\mathbf{1}] > 1.3\times10^5$, only the first (red) and the last (blue) spectra were shown); (B) UV-Visible spectra obtained from solutions of Au@**1** (1.75 μM, red) responding to Cu^{2+} ($[Cu^{2+}]/[Au@\mathbf{1}]=17$, blue), and then responding to Na^+ ($[Na^+]/[Au@\mathbf{1}] > 1.3\times10^5$, black).



(A) (B)

Figure S4. (A) UV-Visible spectra obtained from solutions of Au@**1** (0.4 μM) responding to various concentration of Cs^+ ((a) $[Cs^+]/[Au@\mathbf{1}]=3750$; (b) $[Cs^+]/[Au@\mathbf{1}]=1875$; (c) $[Cs^+]/[Au@\mathbf{1}]=188$; (d) $[Cs^+]/[Au@\mathbf{1}]=19$, V_{THF}: V_{H2O} = 67: 1). The reactions were followed for 1 hour (only the Au@**1** (red line) spectrum was shown). (B) Kinetics for the absorbance at 650 nm for **b**-(●, $k=2.53\times10^{-1}$ s^{-1}), **c**-(●, $k=5.3\times10^{-2}$ s^{-1}) and **d**-(●, $k=4.0\times10^{-2}$ s^{-1}) assemblies (lines: 1st order kinetic fits). Based on the band characteristics and the kinetics of the spectral evolution of the red–shift SP band (*e.g.*, @ 650 nm) (Figure 6 B), apparent rate constants were derived from fitting the time dependence of the absorbance with an exponential growth (k, 1st-order). Under different concentration of $[Cs^+]$, the resulting rate constants displayed an order of **b** (2.53×10^{-1} s^{-1}) > **c** (5.3×10^{-2} s^{-1}) > **d** (4.0×10^{-2} s^{-1}). **a** was quickly precipitated.