Characterization of the Mixed Self-Assembled Monolayer at the Molecular Scale

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Supporting Information

1. Materials and Equipments:

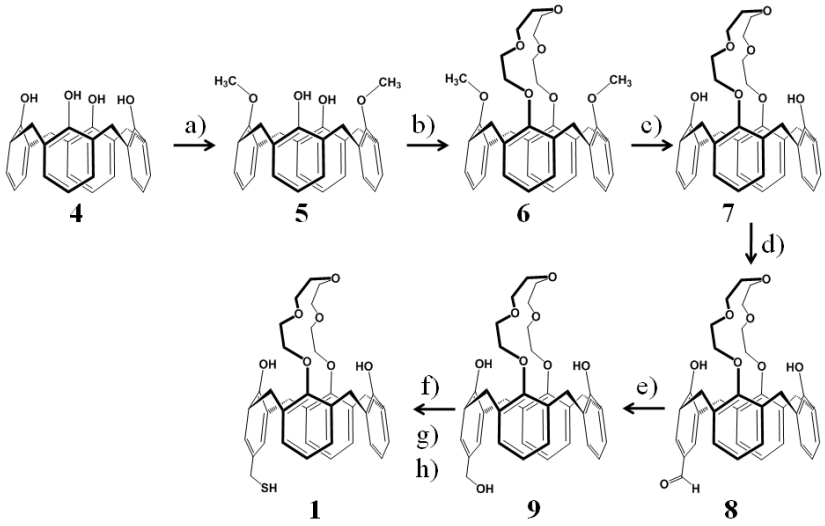
All reagents were obtained from the commercial sources and used as received unless otherwise stated. Receptor **1** and the guest **3** were synthesized according to reported method.[1] Ferrocenecarboxylic acid and tetraethylammonium chloride were purchased from Aldrich and used as received. Gold wire (99.99%, 0.25mm) was purchased from Aldrich. Deionized water was further purified by Barnstead Nanopure system to a final resistivity of 18 MΩ cm. All reactions were carried out under an argon atmosphere unless otherwise indicated. Reactions were monitored by using the thin-layer chromatography (TLC) on Merck Silica Gel 60 F_{254} plates. Visualization of the developed plates was performed under UV light (254 nm) or $KMnO_4$ stain. Organic solutions were concentrated under reduced pressure on a Büchi rotary evaporator.

NMR spectra were recorded on Varian Mercury-300 MHz FT-NMR for ^{1}H NMR spectra. Where ever necessary $CDCl_3$ and D_2O were used as solvents. Data for ^{1}H NMR are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad), coupling constant (Hz), integration.

All the electrochemical experiments were performed with an AFRDE 5 Bi-potentiostat (PINE). Gold bead working electrode, Pt counter electrode and Ag/AgCl reference electrode were fitted in a 10mL, single-compartment electrochemical cell.

2. Scheme for the synthesis of the receptors 1, 17, and guest 3

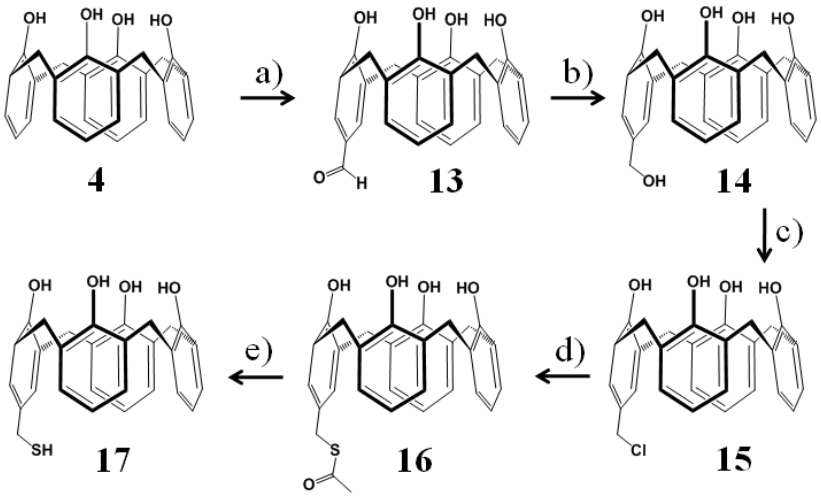
2A. Scheme for the synthesis of the receptor 1



Scheme S1. Synthesis of receptor 1

Reagents and chemicals: a) MeI, K2CO3, 80°C, 7h, 92%; b) $TsO(CH_2CH_2O)_4Ts$, $CsCO_3$, 80°C, 24h, 88%; c) $(CH_3)_3SiI$, 0°C, 0.5h, 93-95%; d) CH_3OCHCl_2 , $SnCl_4$, $CHCl_3$, -15°C, 0.5h, 63%; e) BH_3THF 1M, 0°C. 1h, 86%; f) ClCOCOCl, CH_3Cl, 0°C, 1,5h, 95%; g) $KSOCH_3$, RT, 2h, 90%; h) KOH, MeOH, RT, 1h, 95-96%.

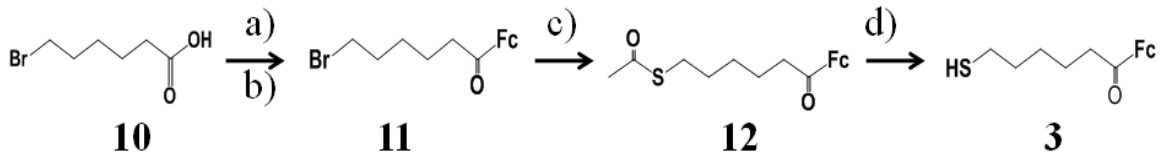
2B. Scheme for the synthesis of the receptor 17



Scheme S2. Synthesis of receptor 17

Reagents and chemicals: a) CH_3OCHCl_2 , $SnCl_4$, $CHCl_3$, -15°C, 0.5h, 65%; b) BH_3THF 1M, 0°C. 1h, 78-80%; c) ClCOCOCl, 0°C, CH_3Cl, 2h, 95-97%; d) $KSCOCH_3$, RT, 2h, 90%; e) KOH, MeOH, RT,1h, 95-96%.

2C. Scheme for the synthesis of the guest 3



10 **11** **12** **3**

Scheme S3. Schematic drawing of synthesis of guest 3.

Reagents and chemicals: a) ClCOCOCl, 0^{o}C, 2h; b) Ferrocene, $AlCl_3$,0^{o}C, 3h, 82-85%; c) $KSCOCH_3$, RT, 2h, 91-94%; d) KOH, MeOH, 1h, 96-98%.

3. Typical procedure for synthesis of compound 1 - 17

3.1. 25, 27-dimethoxy-26,28-dihydroxycalix[4]arene (5)

The 25,26,27,28-tetrahydroxycalix[4] arene **(4)** (3.0 g, 7.07 mmol), MeI (2.5g, 17.70mmol), and K_2CO_3 (9.8 g, 70.70 mmol) were added to the dried CH_3CN (300ml) in the round bottom flask and the mixture was refluxed for 7h at 80°C. Completion of reaction was monitored by TLC (EtOAc: hexane=1:2). Then CH_3CN was moved under reduced pressure and the residue extracted with 100ml of CH_2Cl_2. The organic phase was washed twice with water, separated and dired. The solvent was removed by evaporation, the residue was concentrated and added drop wise to the MeOH (50ml) while stirring. The resulting solid was filtered and dried under vacuum to obtain compound **5** (Yield= 92.5%). (Note: The 25,26,27,28-tetrahydroxycalix[4] arene (4) was obtained by the reported procedure and used here.)

^{1}H NMR ($CDCl_3$, 300 MHz, 298 K) δ (ppm): δ=7.71 (s, 2H, OH), 7.07 (d, J=7.5Hz, 4H, ArH meta), 6.86 (d, J=7.5Hz, 4H, ArH meta) 6.73 (t, J=7.5Hz, 2H, ArH meta), 6.65 (t, J=7.5Hz, 2H, ArH para), 4.29 (d, J=13.2Hz, 4H, $ArCH_2Ar$), 3.97 (s, 6H, OCH_3), 3.39 (d, J=13.2Hz, 4H, $ArCH_2Ar$). ^{13}C NMR (75 MHz, CDCl3, 298K) δ (ppm): δ= 153.3, 153.2, 133.9, 129.2, 128.7, 123.3, 125.5, 119.3, 63.9, 31.5. HR MALDI-TOF: Cal. for $C_{30}H_{28}O_4$ (M+H): m/z = 452.2036. Found: m/z = 452.2046 $[M^+]$, 453.2054 $[M^+ H]^+$.

3.2. 25, 27-dimethoxycalix[4]arene-crown-5 (6)

To the solution of the 26,28-dimethoxy-25,27-dihydroxycalix[4]arene **(5)** (2.9g, 6.40mmol) in CH_3CN (300ml) in the round bottom flask, excess of Cs_2CO_3 (8.15g, 25.00mmol) and tetraethylene glycoldi-p-toluenesulfonate (2.83ml, 7.00mmol) were added under nitrogen atmosphere. The reaction mixture was refluxed for 24h at 80^0C. Completion of reaction was monitored by TLC (EtOAc: hexane=1:2). Then CH_3CN was moved under reduced pressure and the residue extracted with 100ml of CH_2Cl_2. The organic phase was washed twice with water, separated and dired. The solvent was removed by evaporation, the residue was concentrated and added drop wise to the MeOH (50ml) while stirring. The resulting solid was filtered and dried under vacuum to obtain compound **6** (Yield= 88.1%).

^{1}H NMR ($CDCl_3$, 300 MHz, 298 K) δ (ppm): δ=7.13 (d, J=7.3Hz, 4H, ArH meta), 6.90 (t, J=7.3Hz, 2H, ArH para) 6.53 (d, J=7.5Hz, 4H, ArH meta), 6.43 (t, J=7.5Hz, 2H, ArH para), 4.42 (d, J=13.2Hz, 4H, $ArCH_2Ar$), 4.13 (s, 6H, OCH_3), 3.99(m, 4H, $ArOCH_2CH_2OCH_2CH_2$), 3.93 (t, 4H, $ArOCH_2CH_2OCH_2CH_2$), 3.75 (t, 4H, $ArOCH_2CH_2OCH_2CH_2$), 3.58 (t, 4H, $ArOCH_2CH_2OCH_2CH_2$), 3.20 (d, J=13.2Hz, 4H, $ArCH_2Ar$). ^{13}C NMR (75 MHz, CDCl3, 298K) δ (ppm): δ= 159.3, 155.4,

138.9, 136.7, 128.4, 127.7, 122.6, 122.4, 73.0, 71.5, 71.0, 70.8, 61.2, 31.2. HR MALDI-TOF: Cal. for $C_{38}H_{42}O_7$ (M+H): m/z = 610.7394. Found: m/z = 633.3955 $[M^+]Na^+$, 634.3983 $[M^+ H]^+ Na^+$.

3.3. 25, 27-dihydroxycalix[4]arene-crown-5 (7)

25,27-dimethoxycalix[4]arene-crown-5 **(6)** (3.35g, 5.50 mmol**)** was added to the $CHCl_3$ (100 ml) in the round bottom flask and iodotrimethylsilane (1.56ml, 11 mmol) was added the reaction mixture. The reaction mixture was stirred for 0.5 h at 0 ^oC. After completion of reaction the reaction mixture was quenched with 10% HCl (50 ml) and transferred to a separatory funnel. The organic phase was separated and washed with a saturated solution of $Na_2S_2O_3$ and twice with water (2x50ml). $CHCl_3$ was removed under reduced pressure and the product crystallized from MeOH (Yield=93.5%).

^1H NMR ($CDCl_3$, 300 MHz, 298 K) δ (ppm): δ=7.50 (s, 2H, OH), 7.07 (d, J=7.3Hz, 4H, ArH meta), 6.83 (d, J=7.3Hz, 4H, ArH meta) 6.70 (t, J=7.6Hz, 2H, ArH para), 6.68 (t, J=7.5Hz, 2H, ArH para), 4.42 (dd, J=13.1Hz, 4H, $ArCH_2Ar$), 4.15 (t, J=4.8Hz, 4H, $ArOCH_2CH_2OCH_2CH_2$), 4.01 (t, J=4.8Hz, 4H, $ArOCH_2CH_2OCH_2CH_2$), 3.93 (t, J=4.8Hz, 4H, $ArOCH_2CH_2OCH_2CH_2$), 3.84 (t, J=4.8Hz, 4H, $ArOCH_2CH_2OCH_2CH_2$), 3.36 (d, J=13.2Hz, 4H, $ArCH_2Ar$). ^{13}C NMR (75 MHz, CDCl3, 298K) δ (ppm): δ= 153.3, 152.1, 133.1, 128.2, 129.0, 128.5, 125.3, 118.4, 76.4, 71.6, 71.0, 69.9, 31.1. HR MALDI-TOF: Cal. for $C_{36}H_{38}O_7$ (M+H): m/z = 582.6861. Found: m/z = 605.3935 $[M^+]Na^+$, 606.3935 $[M^+ H]^+ Na^+$.

3.4. 11-formyl-25, 27-dihydroxycalix[4]arene-crown-5 (8)

25,27-dihydroxycalix[4]arene-crown-5 **(7)** (5.10mmol) was placed in a dried two-neck round bottom flask under nitrogen atmosphere, and the flask was cooled to -15^oC by the mixture of ice and NaCl (3:1). The $CHCl_3$(100ml), CH_3OCHCl_2(1.38ml, 15.30mmol) were injected sequentially. $SnCl_4$ (17.55ml, 150mmol) was added drop wise into reaction mixture over 0.5h. The mixture was stirred at -15^oC for 0.5h, and then quenched with 10%HCl (50ml) and transferred to a separatory funnel. The organic phase was separated and washed twice with water (50ml). Solvent was removed by evaporation and the residue was concentrated and added drop wise to the MeOH. The resulting solid was filtered and dried under vacuum to obtain compound **8** (Yield= 63%).

^1H NMR ($CDCl_3$, 300 MHz, 298 K) δ (ppm): δ=9.78 (s, 1H, CHO), 8.79 (s, 1H, OH) 7.72 (s, 1H, OH), 7.62 (s, 2H, ArH meta), 7.06 (d, 2H, ArH meta), 6.87 (t, 4H, ArH meta), 6.69 (m, 3H, ArH para), 4.48 (d, J=13.2Hz, 4H, $ArCH_2Ar$), 4.10 (m, 8H, $ArOCH_2CH_2OCH_2CH_2OCH_2CH_2$), 3.93 (t, 4H, $ArOCH_2CH_2OCH_2CH_2OCH_2CH_2$), 3.83 (t, 4H, $ArOCH_2CH_2OCH_2CH_2OCH_2CH_2$), 3.46 (d, J=13.2Hz, 4H, $ArCH_2Ar$). ^{13}C NMR (75 MHz, CDCl3, 298K) δ (ppm): δ= 191.5, 158.1, 155.3,

152.1, 134.1, 130.2, 128.6, 128.2, 127.9, 123.5, 130.3, 125.3, 124.4, 73.4, 71.6, 71.3, 32.1. HR MALDI-TOF: Cal. for C37H38O8 (M+H): m/z = 610.6963. Found: m/z = 633.6457 $[M^+]Na^+$, 634.6478 $[M^+ H]^+ Na^+$.

3.5. 11-hydroxymethyl-25,27-dihydroxycalix[4]arene-crown-5 (**9**)

11-formyl-25, 27-dihydroxycalix[4]arene-crown-5 **(8)** (3.20mmol) was added to the $CHCl_3$ (100ml) in a dried two-neck round bottom flask under nitrogen enviornment, and cooled down to -0°C. BH_3THF 1M (4.80ml, 4.80mmol) was injected drop wise over 5min. The mixture was stirred at 0°C for 1h, and then quenched with 10%HCl (50ml) and then transferred to a separatory funnel. The organic phase was separated and washed twice with water (50ml). Solvent was removed by evaporation and the residue was concentrated and added drop wise to the MeOH. The resulting solid was filtered and dried under vacuum to obtain compound **9** (Yield= 86%).

^{1}H NMR ($CDCl_3$, 300 MHz, 298 K) δ (ppm): δ=7.84 (s, 1H, OH), 7.75 (s, 1H, OH) 7.05 (d, 4H, ArH meta), 6.85 (t, 4H, ArH meta), 6.70 (m, 3H, ArH para), 4.55 (d, 2H, CH_2OH), 4.42 (dd, J=13.2Hz, 4H, $ArCH_2Ar$), 4.09 (m, 8H, $ArOCH_2CH_2OCH_2CH_2OCH_2CH_2$), 3.94 (m, 4H, $ArOCH_2CH_2OCH_2CH_2OCH_2CH_2$), 3.84 (m, 4H, $ArOCH_2CH_2OCH_2CH_2OCH_2CH_2$), 3.36 (d, J=13.2Hz, 2H, $ArCH_2Ar$). ^{13}C NMR (75 MHz, CDCl3, 298K) δ (ppm): δ= 155.3, 152.8, 151.2, 134.0, 128.2, 127.3, 128.2, 127.4, 123.5, 134.1, 125.2, 124.2, 73.4, 71.6, 71.2, 65.1, 32.5 32.2. HR MALDI-TOF: Cal. for $C_{37}H_{40}O_8$ (M+H): m/z = 612.7122. Found: m/z = 635.6972 $[M^+]$ Na^+, 636.6987 $[M^+ H]^+ Na^+$.

3.6. 11-mercaptomethyl-25,27-dihydroxycalix[4]arene-crown-5 (1)

11-hydroxymethyl-25,27-dihydroxycalix[4]arene-crown-5 **(9)** (2.75mmol) was added to the $CHCl_3$ (100ml) in a dried two-neck round bottom flask under nitrogen enviornment, and cooled down to -0°C. Oxalyl chloride (0.30ml, 3.5mmol) was added drop wise to the reaction mixture over 5min. The mixture was stirred at 0°C for 2 more hours, and then quenched with 5ml 10%HCl and then water (50ml) was added. The mixture was then transferred to a separatory funnel, the organic phase was separated and washed twice with water (50ml). Solvent was removed by evaporation and the residue was concentrated and added drop wise to the MeOH. The resulting solid was filtered and dried under vacuum (yield 95.9%) and used for next step without futher purification.

The dried compound (2.6mmol) obtained in previous step was added to the mixture of $KSCOCH_3$ (0.90g, 7.8mmol) and CH_3OCH_3(50ml) in the round bottom flask, and sonicated at room temperature for 2h. The mixture was evaporated under reduced pressure to remove solvent. The residuce was dissolved in $CHCl_3$ (50ml), quenched with 1M HCl (50ml) and then transferred to a separatory funnel. The organic phase was separated and washed twice with water (50ml). Solvent

was removed by evaporation and the residue was concentrated and added drop wise to the MeOH. The resulting solid was filtered and dried under vacuum (yield 90.8%) and used for next step without futher purification.

The dried compound (2.30mmol) obtained in previous step was added to the mixture of CH_2Cl_2 and CH_3OH (5:1, 50ml) in the round bottom flask. 1M KOH (0.5ml) was added to the mixture and the obtained mixture was sonicated for 1h at room temperature. The solvents were evaporated under reduced pressure, the resudue was dissolved in CH_2Cl_2(50ml) and quenched with 1M HCl (50ml) and then transferred to a separatory funnel. The organic phase was separated and washed twice with water (50ml). Solvent was removed by evaporation and the residue was concentrated and added drop wise to the MeOH. The resulting solid was filtered and dried under vacuum to obtain compound **1** (Yield= 96.7%).

^{1}H NMR ($CDCl_3$, 300 MHz, 298 K) δ (ppm): δ=7.75 (s, 2H, OH), 7.06 (d, 4H, ArH meta), 6.86 (d, 4H, ArH meta), 6.68 (m, 3H, ArH para), 4.41 (d, J=12.9Hz, 4H, $ArCH_2Ar$), 4.09 (s, 8H, $ArOCH_2CH_2OCH_2CH_2OCH_2CH_2$), 3.95 (t, 4H, $ArOCH_2CH_2OCH_2CH_2OCH_2CH_2$), 3.84 (t, 4H, $ArOCH_2CH_2OCH_2CH_2OCH_2CH_2$), 3.66 (s, 2H, CH_2SH), 3.36 (d, J=13.2Hz, 2H, $ArCH_2Ar$). ^{13}C NMR (75 MHz, CDCl3, 298K) δ (ppm): δ= 159.1, 155.4, 151.2, 136.1, 134.2, 132.5, 132.9, 132.1, 128.7, 134.0, 128.7, 127.5, 73.4, 71.6, 71.0 61.5, 31.5, 31.2. HR MALDI-TOF: Cal. for $C_{37}H_{40}O_7S$ (M+H): m/z = 628.7783. Found: m/z = 651.7734 $[M^+]$ Na^+, 651.7756 $[M^+ H]^+$ Na^+.

3.7. 5-formyl-25,26,27,28-tetrahydroxycalix[4]arene (13)

The 25,26,27,28-tetrahydroxycalix[4] arene **(4)** (5.10mmol) was placed in a dried two-neck round bottom flask under nitrogen enviornment, and cooled to -15^{o}C by mixture of ice and NaCl (3:1). Then $CHCl_3$(100ml), CH_3OCHCl_2(1.38ml, 15.30mmol) were sequentially injected into the flask. $SnCl_4$ (17.55ml, 150mmol) was added drop wise into reaction mixture over 0.5h. The mixture was stirred at -15^{o}C for 0.5h, and then quenched with 10%HCl (50ml) and transferred to a separatory funnel. The organic phase was separated and washed twice with water (50ml). Solvent was removed by evaporation and the residue was concentrated and added drop wise to the MeOH. The resulting solid was filtered and dried under vacuum to obtain compound **13** (Yield= 63.6%).

^{1}H NMR ($CDCl_3$, 300 MHz, 298 K) δ (ppm): δ=9.78 (s, 1H, CHO), 10.25 (s, 4H, OH), 7.63 (s, 2H, ArH meta), 7.08 (t, 2H, ArH meta), 7.04 (d, 4H, ArH meta), 6.73 (m, 3H, ArH para), 4.26 (s, 4H, $ArCH_2Ar$), 3.54 (s, J=13.2Hz, 4H, $ArCH_2Ar$). ^{13}C NMR (75 MHz, CDCl3, 298K) δ (ppm): δ= 190.2, 158.3, 152.1, 130.1, 128.2, 128.5, 130, 125.3, 31.5. HR MALDI-TOF: Cal. for $C_{29}H_{24}O_5$ (M+H): m/z = 452.5012. Found: m/z = 452.5134 $[M^+]$, 453.5156 $[M^+ H]^+$.

3.8. 5-hydroxymethyl-25,26,27,28-tetrahydroxy calix[4]arene (14)

11-formyl-25,26,27,28-tetrahydroxycalix[4]arene **(13)** (3.20mmol) was added to the $CHCl_3$ (100ml) in a dried two-neck round bottom flask under nitrogen enviornment, and cooled down to -0°C. BH_3THF 1M (4.80ml, 4.80mmol) was added drop wise to the reaction mixture over 5min. The mixture was stirred at 0°C for 1h, quenched with 10%HCl (50ml) and then transferred to a separatory funnel. The organic phase was washed twice with water (50ml). Solvent was removed by evaporation and the residue was concentrated and added drop wise to the MeOH. The resulting solid was filtered and dried under vacuum to obtain compound **14** (Yield=86.4%).

^{1}H NMR ($CDCl_3$, 300 MHz, 298 K) δ (ppm): δ=10.19 (s, 4H, OH), 7.08 (s, 2H, ArH meta), 7.05 (d, 6H, ArH meta), 6.73 (m, 3H, ArH para), 4.47 (d, 2H, CH_2OH), 4.26 (dd, J=13.2Hz, 4H, $ArCH_2Ar$), 3.54 (d, J=13.2Hz, 2H, $ArCH_2Ar$), 1.41 (t, 1H, OH); ^{13}C NMR (75 MHz, CDCl3, 298K) δ (ppm): δ= 152.3, 151.2, 128.3, 127.2, 128.1, 127.0, 134.5, 125.1, 65.1, 31.5. HR MALDI-TOF: Cal. for $C_{29}H_{24}O_5$ (M+H): m/z = 454.5164. Found: m/z = 454.5178 [M^+], 455.5123 [M^+ H]$^+$.

3.9. 5-chloromethyl-25,26,27,28-tetrahydroxy calix[4]arene (15)

5-hydroxymethyl-25,26,27,28-tetrahydroxycalix[4]arene (**14**) (2.75mmol) was added to the $CHCl_3$ (100ml) in a dried two-neck round bottom flask under nitrogen atmosphere, and cooled down to -0°C. Oxalyl chloride (0.30ml, 3.5mmol) was drop wise injected to the reaction mixture over 5min. The mixture was stirred at 0°C for 2 more hours, and then quenched with water (50ml) and then 5ml 10%HCl was added to it. The reaction mixture was transfered to the seperatory funnel and the organic phase was washed twice with water (50ml). Solvent was removed by evaporation and the residue was concentrated and added drop wise to the MeOH. The resulting solid was filtered and dried under vacuum to obtain compound **15** (Yield= 95.68%).

^{1}H NMR ($CDCl_3$, 300 MHz, 298 K) δ (ppm): δ=10.19 (s, 4H, OH), 7.06 (s, 2H, ArH meta), 7.04 (d, 6H, ArH meta), 6.72 (m, 3H, ArH para), 4.48 (s, 2H, CH_2Cl), 4.26 (dd, J=13.2Hz, 4H, $ArCH_2Ar$), 3.54 (d, J=13.2Hz, 2H, $ArCH_2Ar$). ^{13}C NMR (75 MHz, CDCl3, 298K) δ (ppm): δ= 152.3, 152.0, 128.5, 127.3, 128.2, 127.0, 131.4, 125.0, 46.5, 32.3, 31.8. HR MALDI-TOF: Cal. for $C_{29}H_{25}ClO_4$ (M+H): m/z = 472.9622. Found: m/z = 472.8988 [M^+], 473.8934 [M^+ H]$^+$.

3.10. 5-Thioacetylmethyl-25,26,27,28-tetrahydroxy calix[4]arene (16)

5-chloromethyl-25,26,27,28-tetrahydroxy calix[4]arene (**15**) (2.6mmol) and $KSCOCH_3$ (0.90g, 7.8mmol) were added to the CH_3OCH_3(50ml) in the round bottom flask and the mixture was sonicated at room temperature for 2h. The solvent was evaporated under reduced pressure to remove and the residuce was dissolved in $CHCl_3$ (50ml), quenched with 1M HCl (50ml) and then transferred

to a separatory funnel. The organic phase was separated and washed twice with water (50ml). Solvent was removed by evaporation and the residue was concentrated and added drop wise to the MeOH. The resulting solid was filtered and dried under vacuum to obtain compound **16** (Yield= 99.21%).

^{1}H NMR ($CDCl_3$, 300 MHz, 298 K) δ (ppm): δ=10.18 (s, 4H, OH), 7.07 (s, 2H, ArH meta), 7.03 (d, 6H, ArH meta), 6.70 (m, 3H, ArH para), 4.58 (s, 2H, CH_2SCO), 4.26 (dd, J=13.2Hz, 4H, $ArCH_2Ar$), 3.54 (d, J=13.2Hz, 2H, $ArCH_2Ar$), 2.35 (s, CH_3COS); ^{13}C NMR (75 MHz, CDCl3, 298K) δ (ppm): δ= 195.2, 151.6, 150.3, 128.3, 127.6, 128.0, 127.3, 132.4, 123.0, 33.5, 32.3, 31.8, 30.8. HR MALDI-TOF: Cal. for $C_{31}H_{28}O_5S$ (M+H): m/z = 512.6193. Found: m/z = 512.6135 [M^+], 513.6189 [M^+ H]$^+$.

3.11. 5-mecaptomethyl-25,26,27,28-tetrahydroxy calix[4]arene (17)

5-Thioacetylmethyl-25,26,27,28-tetrahydroxy calix[4]arene (**16**) (2.30mmol) was dissolved in mixture of CH_2Cl_2 and CH_3OH (5:1, 50ml). 1M KOH (0.5ml) were added and sonicated for 1h at room temperature. The solvents were evaporated under reduced pressure before dissolved again in CH_2Cl_2(50ml), quenched with 1M HCl (50ml) and then transferred to a separatory funnel. The organic phase was separated and washed twice with water (50ml). Solvent was removed by evaporation and the residue was concentrated and added drop wise to the MeOH. The resulting solid was filtered and dried under vacuum to obtain compound **17** (Yield= 95.56%).

^{1}H NMR ($CDCl_3$, 300 MHz, 298 K) δ (ppm): δ=10.18 (s, 3H, OH), δ=10.14 (s, 1H, OH), 7.04 (d, 4H, ArH meta), 7.04 (t, 2H, ArH meta), 6.89 (s, 2H, ArH meta), 6.71 (m, 3H, ArH para), 4.24 (s, 4H, $ArCH_2Ar$), 3.48 (d, 2H, CH_2SH), 3.54 (s, 2H, $ArCH_2Ar$). ^{13}C NMR (75 MHz, CDCl3, 298K) δ (ppm): δ= 148.9, 148.4, 129.2, 128.6, 128.4, 128.2, 131.0, 122.5, 61.5, 32.1. HR MALDI-TOF: Cal. for $C_{29}H_{26}O_4S$ (M+H): m/z = 470.5825. Found: m/z = 469.5783 [M^-], 470.5733 [M^+], 471.5485 [M^+ H]$^+$.

3.12. 6-bromohexanoyl ferrocenecarboxylate (11)

6-bromohexanoic acid **(10)** (3.0g, 15.0mmol) was added to the $CHCl_3$ (30ml) taken in round bottom flask under nitrogen atmostphere, and cooled down to -0^{o}C. ClCOCOCl (1.93ml, 22.5mmol) was injected drop wise to the reaction mixture over 15min. The mixture was stirred at 0^{o}C for 2 more hours and then solvent was evaporated under reduced pressure. The crude product (6-bromohexanecarboxyl chloride) was directly used for the next step without further purification.

The flask containing 6-bromohexanecarboxyl chloride (3.44g, 15.0mmol) was firstly cooled down to 0^{o}C and to it ferrocene (2.79g, 15mmol) and $AlCl_3$ (6.0g, 45.0mmol) was added. The

reaction was continued for 3h then quenched with 10%HCl (50ml), the obtained precipitate was separated by filtration and then re-crystallized from C_2H_5OH/H_2O (2:1) to obtain compound **11** (Yield= 82.56%).

^{1}H NMR ($CDCl_3$, 300 MHz, 298 K) δ (ppm): δ= 4.77 (t, 2H, Fc), 4.49 (t, 2H, Fc), 4.19 (s, 5H, Fc), 3.45 (t, 2H, CH_2Br), 2.73 (t, 2H, $FcCOCH_2$), 1.94 (q, 2H, $BrCH_2CH_2$), 1.74 (q, 2H, $FcCOCH_2CH_2CH_2$) 1.52 (q, 2H, $FcCOCH_2CH_2CH_2$). ^{13}C NMR (75 MHz, CDCl3, 298K) δ (ppm): δ= 204.4, 141.2, 138.0, 126.5, 38.5, 33.2, 32.8, 28.6, 27.3. HR MALDI-TOF: Cal. for $C_{16}H_{19}BrFeO$ (M+H): m/z = 363.0722. Found: m/z = 363.1128 [M^+], 364.2356 [M^+ H]$^+$.

3.13. Synthesis of 6-thioacetylhexanoyl ferrocenecarboxylate (12)

6-bromohexanoyl ferrocenecarboxylate (**11**) (4.55g, 12mmol) and $KSCOCH_3$ (4.1g, 36mmol) were added to the CH_3OCH_3 (50ml) taken in round bottom flask and sonicated at room temperature for 2h. The mixture was evaporated under reduced pressure to remove solvent. The residuce was dissolved in $CHCl_3$ (50ml), quenched with 1M HCl (50ml) and then transferred to a separatory funnel. The organic phase was separated and washed twice with water (50ml). Solvent was removed by evaporation and and the product was re-crystalized from C_2H_5OH/H_2O (2:1) to obtain compound **12** (Yield= 91.34%).

^{1}H NMR ($CDCl_3$, 300 MHz, 298 K) δ (ppm): δ= 4.77 (t, 2H, Fc), 4.49 (t, 2H, Fc), 4.19 (s, 5H, Fc), 2.90 (t, 2H, $AcSCH_2CH_2$), 2.70 (t, 2H, $FcCOCH_2CH_2CH_2$), 2.34 (s, CH_3COS), 1.74 (q, 2H, $FcCOCH_2CH_2CH_2$), 1.63 (q, 2H, $AcSCH_2CH_2CH_2$) 1.45 (q, 2H, $FcCOCH_2CH_2CH_2$).. ^{13}C NMR (75 MHz, CDCl3, 298K) δ (ppm): δ= 204.5, 196.9, 141.3, 138.2, 126.7, 38.2, 29.7, 29.7, 28.6, 24.2. HR MALDI-TOF: Cal. for $C_{18}H_{22}FeO_2S$ (M+H): m/z = 358.2784. Found: m/z = 358.3024 [M^+], 359.3216[M^+ H]$^+$.

3.14. Synthesis of 6-mercapto hexanoyl ferrocenecarboxylate (3)

6-thioacetylhexanoyl ferrocenecarboxylate **(12)** (3.74g, 10mmol) was added to the CH_3OH taken in round bottom flask under nitrogen environment. 1M KOH (0.5ml) was added to the reaction mixture and sonicated for 1h at room temperature. The solvent was evaporated under reduced pressure and the residue was issolved in CH_2Cl_2(50ml), quenched with 1M HCl (50ml) and then transferred to a separatory funnel. The organic phase was separated and washed twice with 50ml water. Solvent was removed by evaporation and and the product was re-crystalized from C_2H_5OH/H_2O (2:1) to obtain compound **3** (Yield= 95.96%).

^{1}H NMR ($CDCl_3$, 300 MHz, 298 K) δ (ppm): δ= 4.77 (t, 2H, Fc), 4.49 (t, 2H, Fc), 4.19 (s, 5H, Fc), 2.71 (t, 2H, $FcCOCH_2$), 2.64 (s, 1H, SH), 2.56 (q, 2H, $HSCH_2$), 1.8~1.6 (m, 4H, $HSCH_2CH_2$ +

$FcCOCH_2CH_2$), 1.49 (m, 2H, -CH_2-). ^{13}C NMR (75 MHz, CDCl3, 298K) δ (ppm): δ= 204.8, 141.2, 138.0, 126.5, 39.2, 31.8, 28.7, 24.7, 24.2. HR MALDI-TOF: Cal. for $\mathbf{C}_{16}H_{20}FeOS$ (M+H): m/z = 316.2416. Found: m/z = 316.2567 [M^+], 317.2478 [M^+ H]$^+$.

4. Fabrication and characterization of the SAM of the monothiolated calix[4]crown-5 receptor 1:

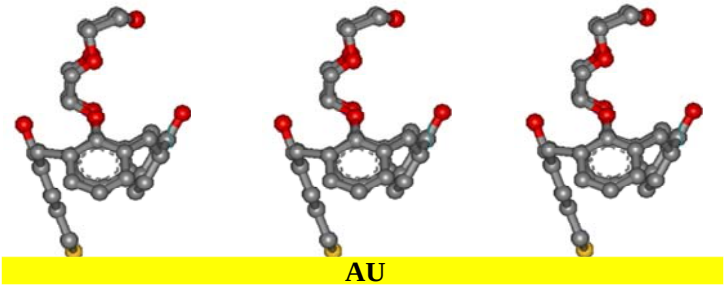


Figure S1: Self-assembled monolayer of the monothiolated calix[4]crown-5 receptor 1

The gold bead working electrodes were obtained by following the reported procedures.[2] The estimation of geometry areas of gold beads by following these reports varied in the range of 0.06 cm±0.005cm^2. After its preparation, the gold bead was etched in piranha solution for 3min, washed three times by deionized water and then dried completely under the environment of the N_2 gas. The gold bead was immersed in 1mM solution of the receptor **1** in the chloroform for 4hr and rinsed sequentially with $CHCl_3$, acetone, ethanol, and 150mM NaCl solution.[3]

The interfacial complexation phenomena between the ferrocenecarboxylate (Fc-COO^-) guest and the anchored calix[4]crown-5 receptor **1** was studied by Cyclic Voltammetry (CV). The first CV was recorded in 10mM Et_4NCl solution in the presence of 0.1mM ferrocenecarboxylate, scan rate was 100mV/s. The second CV scan was consecutively recorded after 1min under the similar conditions.

5. Fabrication and characterization of the mixed SAM (receptor 1 and guest 3) modified gold electrode:

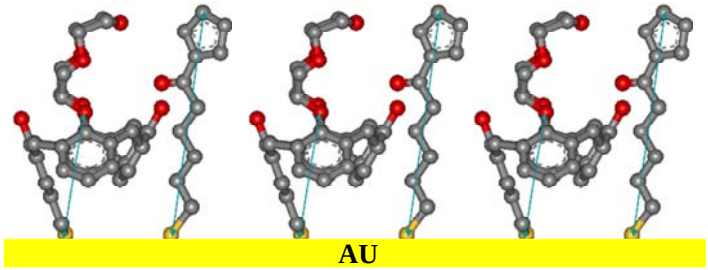


Figure S2: Mixed self-assembled monolayer of the monothiolated calix[4]crown-5 (1) and the thiolated alkylferrocene (3)

After pre-treating with piranha solution as previous experiment, the coating process of gold beads was performed firstly in 1mM solution of **1** in chloroform for 20min. After rinsing several times with chloroform, the above coating electrode was immediately immersed in the 1mM solution of **3** for 4h, and then rinsed sequentially with $CHCl_3$, acetone, ethanol, and 150mM NaCl solution to obtain the well-defined mixed SAM of the receptor **1** and guest **3**. In order to characterize the interfacial properties of the obtained electrodes, two consecutive CVs (the first and second CVs) were recorded in the 10mM solution of the Et_4NCl, scan rate was 0.1V/s; the interval between two CVs was 1min.

The **Figure S3A** demonstrates that in case of the formation of islands during the construction of the mixed SAM are not suitable for interaction between receptor **1** and guest **3**. Therefore, based on the cyclic voltammograms it is clear that the receptor **1** and guest **3** tend to form well-defined mixed SAM as shown in the **Figure S3B**.

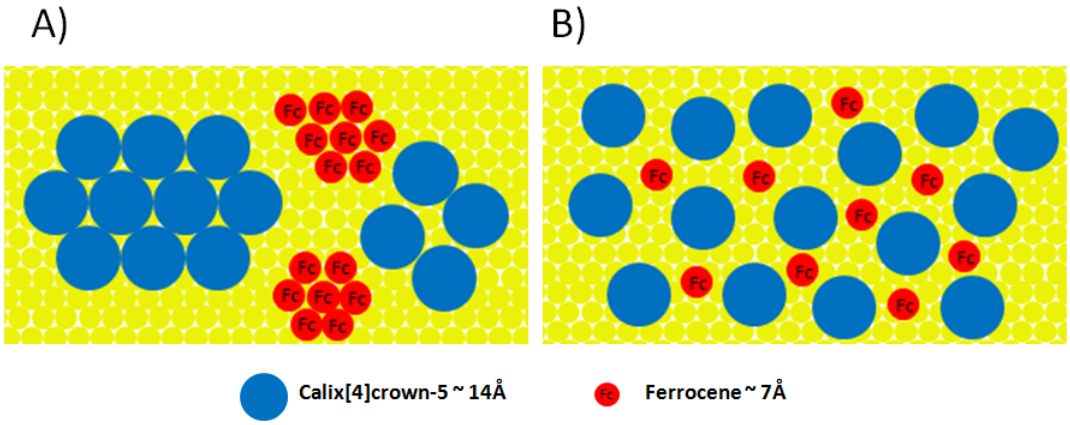


Figure S3: The schematic drawing of the mixed SAM of the receptor 1 and the guest 3 on the surface of the gold electrode

6. Competition experiment:

Effect of the NH_4Cl on the third CV of the mixed SAM was studied. The mixed SAM modified electrodes after performing first and second CVs were used in this experiment. In the third CV, only NH_4^+Cl was added with final concentration of 500mM, while other conditions were not changed. After the third CV was recorded, the working electrode was then washed several times with deionized water to remove the complexed NH_4^+ ions with the receptor **1**. The fourth and fifth CVs were then performed in 10mM Et_4NCl solution (without NH_4^+) in order to compare the results with the first and second CVs, respectively. The scan rate was fixed at 0.1V/s. The duration between each CV scan is 1 minute.

7. Coverage (Γ_{Fc}) of guest 3 on the surface of the gold electrode

The coverage (Γ_{Fc}) of guest **3** on the surface of the gold electrode modified with the SAM of receptor **1** was calculated from the following equation[4]:

$$A_p = Q = nvF\Gamma A_e \rightarrow \Gamma = Q/(nvFA_e)$$

Where:

A_p is peak area (V * A)
A_e is surface area of the gold electrode, (~ 0.06±0.004cm^2)
Γ is surface coverage (mol/cm^2)
v is sweep rate =0.10V/s
F is Faraday Constant (96485 s.A/mol)

8. Interaction of the monothiolated calix[4]arene receptor 17 anchored on the gold surface and the ferrocenecarboxylate guest 2.

Figure S4 demonstrates that the monothiolated calix[4]arene receptor **10** (without crown-5 moiety) did not show any interaction with the guest **2**, ruling out any possibility of the chemical binding or physical adsorption during the interaction of the receptor **1** with guest **2** or **3**.

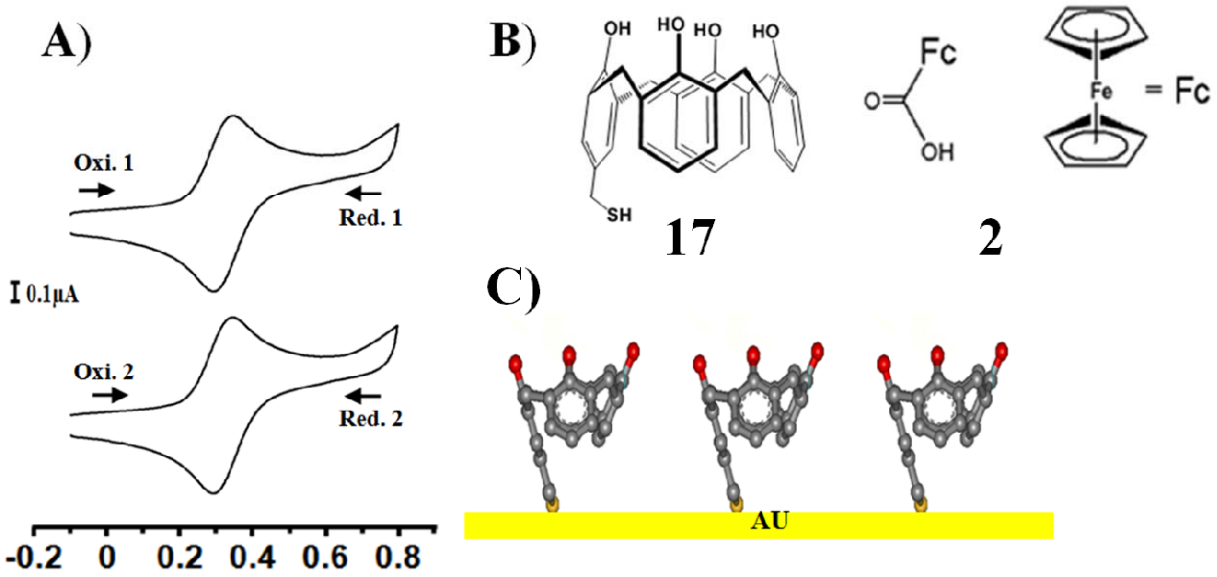


Figure S4: **Interaction of the monothiolated calix[4]arene 17 anchored on the gold surface and the ferrocenecarboxylate (2) in the solution.** A) First and Second consecutive cyclic voltammograms of the gold electrode modified with the SAM of monothiolated calix[4]aren in the presence of the 0.1mM guest **2** in 10mM Et_4NCl solution, scan rate of 0.1V/s, B) The monothiolated calix[4]arene receptor **17** and guest **2**, C) Self-assembled monolayer of the monothiolated calix[4]arene receptor **17**.

9. Interaction of the monothiolated calix[4]arene receptor 17 anchored on the gold surface and the anchored thiolated alkylferrocene 3.

The mixed self-assembled monolayer of the monothiolated calix[4]crown-5 **17** and the thiolated alkylferrocene **3** was prepared by following the method mentioned for the mixed-SAM of receptor **1** and guest **3. Figure S5** demonstrates that the monothiolated calix[4]arene receptor **17** (without crown-5 moiety) did not show any interaction with the guest **3**, ruling out any possibility of the chemical binding or physical adsorption during the interaction of the receptor **1** with guest **3**.

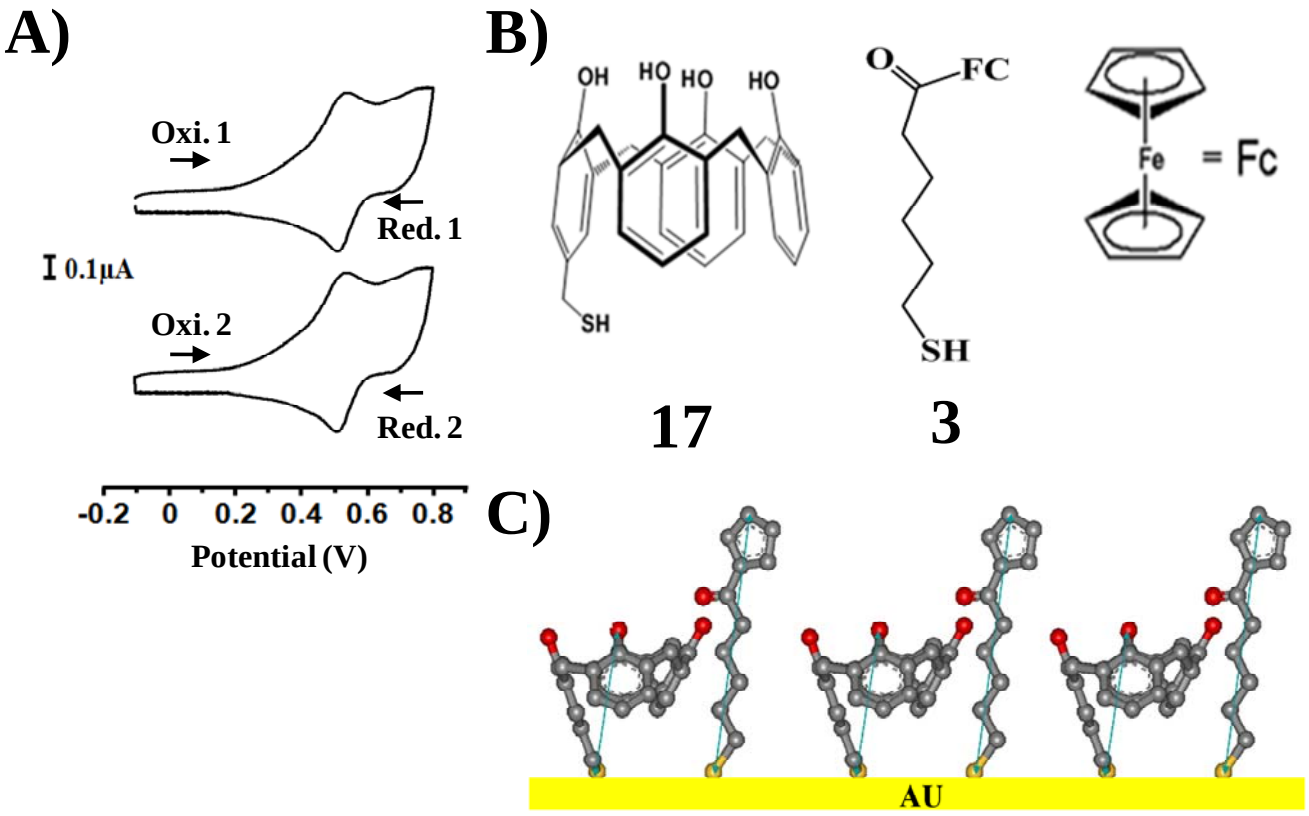


Figure S5: **Interaction of the receptor 1 and guest 3 in the mixed SAM on the gold surface.** A) First and Second consecutive cyclic voltammograms of the gold electrode modified with the mixed-SAM of the receptor **17** and guest **3**. B) The monothiolated calix[4]arene receptor **17** and guest **3**, C) Mixed self-assembled monolayer of the monothiolated calix[4]arene receptor **17** and guest **3**.

10. References:

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[2] Y. Wang, A. E. Kaifer, J. Phys. Chem. B, **1998,** 102, 9922-9927.

[3] H. S. Jung, K. S. Song, T. S. Kim, Bull. Korean Chem. Soc. **2007**, 28, 1792-1796.

[4] J. Wang, *Analytical Electrochemistry*, Wiley-VCH, New York, **2006**, p. 123.