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1. Synthetic procedure:

1.1. Microwave assisted synthesis of p-tert-butylcalix[4]arene,1

The procedure was essentially the same as those developed by Menon et al1 with minor modification. A mixture of p-tert-butyl phenol (4.0 g, 0.33 mM), sodium hydroxide (NaOH)(1 g) and formaldehyde(1.8 ml,0.18 mM) solution was taken in an open vessel and was irradiated with 50 W power in a microwave synthesizer Discover(CEM) by stirring for 3 min. After cooling for 10 min, resulted yellow solid mass. Next, 4 ml of toluene and 30 ml of diphenyl ether was added in this yellow solid, again irradiated with microwave power of 100 W for 5 min with stirring and obtained a dark brown solution. Further, this solution was added in to 75 ml of ethyl acetate and kept for 2 h. Finally, white precipitate was obtained which was filtered and washed with ethyl acetate and finally dried. Yield,3.5g(96%).Elemental analysis for C_{44}H_{56}O_{4}, Calcd. C;81.44%, H; 8.70%, O; 9.80%, Found:C;80.11%,H; 8.26%,O;9.90%1HNMR: δ_{H}(CDCl_{3},400MHZ):1.28(36H,s,tBu), 3.81(8H.s, ArCH_{2}Ar), 7.12(8H,s,Ar-H), 9.61(4H,s,Ar-OH). FAB MS(m/z)648 (M+1).


A mixture of p-tert-butylcalix[4]arene 1 (3.5 g, 0.005 mol ), K_{2}CO_{3}(1.9 g, 1.0 mol ) and 1-bromoethane (4 ml, 1.0 mol) in dry acetonitrile (150 ml) was stirred for 24 hrs. The actual reaction time was considered by taking TLC at regular interval of time by using mixture of (ethylacetate:hexane, 8:2).The solvent was then evaporated under vacuum and the residue taken up with CH_{2}Cl_{2}. The organic phase was washed with 0.1 M HCl up to neutrality and dried over anhydrous Na_{2}SO_{4}. After complete evaporation of the solvent, the resulting crude product was purified by column chromatography (silica gel, hexane9: ethyl acetate 1); 2.9 g, yield(81%).Elemental analysis for C_{50}H_{70}O_{6}, Calcd.C;81.77%,H;9.15%,O;9.08% Found:C;81.42%,H;9.01%,O;9.03%.1HNMR: δ_{H}(DMSO,400MHZ);1.12(18H,t,Bu), 0.86 (18H,t-butyl,s),4.21(4H,-OCH_{2}t),3.61(H,-OCH_{2}t),3.08(4H,ArCH_{2}Ar,d),3.77(4H,OCH_{2}s), 4.21(4H,
ArCH₂Ar, d), 6.21 (4H, Ar-H, s), 6.15 (4H, Ar-H, s), 8.11 (2H, OH, s), m.p. >250 °C. ESI-MASS (m/z) 706 (M+1).

A mixture of p-tert-butylcalix[4]arene 1 (2.9 g, 0.005 mol), K₂CO₃ (1.9 g, 1.0 mol) and 2 chloroethoxyethanol (4 ml, 1.0 mol) in dry acetonitrile (150 ml) was stirred for 24 hrs. The actual reaction time was considered by taking TLC at regular interval of time by using mixture of (ethyl acetate : hexane, 8:2). The solvent was then evaporated under vacuum and the residue taken up with CH₂Cl₂. The organic phase was washed with 0.1 M HCl up to neutrality and dried over anhydrous Na₂SO₄. After complete evaporation of the solvent, the resulting crude product was purified by column chromatography (silica gel, hexane: ethyl acetate 1); 2.7 g, yield (97%). Elemental analysis for C₅₂H₇₂O₆, Calcd. C; 78.75%, H; 9.15%, O; 12.10%. Found: C; 78.61%, H; 9.08%, O; 11.97%. ¹H NMR: δ H(DMSO, 400 MHz): 1.20 (18H, t-butyl, s), 0.96 (18H, t-butyl, s), 4.28 (8H, -OCH₂, t), 3.21 (4H, -OCH₂CH₂OH, t), 1.94 (6H, CH₂CH₃, t), 3.18 (4H, ArCH₂Ar, d), 4.30 (4H, ArCH₂Ar, d), 6.42 (4H, Ar-H, s), 6.85 (4H, Ar-H, s), 8.89 (2H, OH, s), m.p. >250 °C. ESI-MASS (m/z) 794 (M+1).

A mixture of compound C (2.3 g, 0.004 mol), K₂CO₃ (1.9 g, 0.0085 mol) and dibromoethane (4 ml, 0.008 mol) in dry acetonitrile (150 ml) was stirred for 24 hrs. Elemental analysis for C₅₆H₇₈Br₂O₆, Calcd. C; 66.79%, H; 7.81%, O; 9.53%, Br; 15.87%. Found: C; 66.13%, H; 7.48%, O; 9.37%, Br; 15.47%. ¹H NMR: δ H(DMSO, 400 MHz): 0.96 (18H, t-butyl, s), 4.28 (8H, -OCH₂, t), 3.21 (4H, -OCH₂CH₂OH, t), 1.94 (6H, CH₂CH₃, t), 3.18 (4H, ArCH₂Ar, d), 4.30 (4H, ArCH₂Ar, d), 6.12 (4H, Ar-H, s), 6.35 (4H, Ar-H, s), m.p. >250 °C. FAB MASS (m/z) 1008 (M+1).

To 40-mL of acetonitrile having 2.0 g of D, 0.28 g (3.65 mmol) of thiourea was added and the resultant mixture was heated under reflux overnight. Acetonitrile was then removed under reduced pressure. The resulting solid product was mixed with 0.37 g (6.59 mmol) of KOH and an aliquot of 40 mL of deionized water. The mixture was refluxed for 2 h. The compound formed was extracted with 1 M HCl and CH₂Cl₂, dried with MgSO₄(s), and purified with column chromatography (SiO₂, hexane/EtOAc 1:3). Yield 1.7 g. 85% Elemental analysis for C₅₆H₇₈S₂O₆, Calcd. C; 73.64%, H; 8.83%, O; 10.51%, S; 7.02%. Found: C; 73.31%, H; 8.51%, O; 10.17%, S; 6.97%. ¹H NMR: δ H(DMSO, 400 MHz): 1.71 (18H, t-butyl, s), 1.11 (18H, t-butyl, s), 4.12 (8H, -OCH₂, t), 3.41 (8H, -OCH₂, s), 3.11 (4H, -OCH₂CH₂OH, t), 1.14 (6H, CH₂CH₃, t), 3.01 (4H, ArCH₂Ar.

A solution of 4(1.7 g, 0.65 mmol) in 5 mL of sulphuric acid (96%) was stirred at 80°C for 5 h. An aliquot was withdrawn from the solution and poured in to water to determine the progress of the reaction. The reaction was completed when water insoluble material was not detected. After cooling the precipitate was separated by filtration. The precipitate was dissolved in 8 mL of water before addition of 20 mL BaCO₃ solution for neutralization. Precipitated BaSO₄ was removed by filtration. The product was obtained after evaporation of water in the filtrate. The product was dried in a high vacuum oven. Yield 1.5g(90%) Elemental analysis for C₄₀H₄₈S₆O₁₈, Calcd. C; 47.61%, H;4.79%, O;28.54, S;19.06% Found:C;47.22%, H;4.71%, O;28.11%, S;19.01.¹HNMR: δ(H(DMSO, 400MHZ): 1.88(18H,t-butyl,s,) 1.16(18H,t-butyl,s) 4.28(8H,-OCH₂,t) 3.12(8H,-OCH₂,s), 3.33(4H,-OCH₂CH₂OH,t) 1.94(6H,-CH₂CH₃,t) 3.08(4H, ArCH₂Ar,d), 1.51(2H,-SH,s), 4.30(4H, ArCH₂Ar,d), 6.42(4H, Ar-H, s), 6.85(4H, Ar-H, s), m.p. >250 °C. ESI MASS (m/z) 1009 (M+1).

1.7. Microwave synthesis of silver nanoparticles:

The procedure was essentially the same as those developed by Menon et al¹ with minor modification. The molar ratio of silver nitrate to sodium citrate also has been changed accordingly. All glassware was thoroughly cleaned with freshly prepared 3:1 HCl/HNO₃ (aqua regia) and rinsed thoroughly with Milli-Q water prior to use. The synthesis was carried out in a modified CEM Discover microwave using single mode and continuous power at 2.45 GHz. The reactions were carried out in sealed reaction vessel containing 3 ml of 0.25 mM AgNO₃ solution and 2 ml of 13 mM sodium citrate and was heated at 80 °C at a power up to 100 W for 4 min. The solution changed from colorless to vivid yellow yield Ag nanoparticles of ~ 40 nm.

1.8 Preparation of Blood sample:

For this study 4 healthy subject’s median cubital and cephalic veins of the arm punctured with a sterile needle attached to an aspirating device. Collected 5 ml blood dispensed in 25 ml of RBC lysis buffer, the sample kept at room temperature for 10 to 15 minutes then centrifuged the solution at 10,000 rpm for 10 minutes. Aspirated the supernatant from resultant solution, in another sterile test-tube and added the ascorbic acid to set the pH range between 4.5-5.
**Fig. S1** Transmission IR spectra of (A) pSTEC₄ (B) pSTEC₄ modified silver nanoparticles (disappearance of the S-H stretching in the pSTEC₄-AgNPs as indicated by arrow).

**Fig. S2** Shows the response behaviour after addition of 10 μM ferric ion in 0.15 mM pSTEC₄-AgNPs
Fig. S3 The relative absorbance change of pSTEC₄-AgNPs solutions after adding 10μM different metal ions from left to right (A) Zn²⁺, Fe³⁺, Cu²⁺, Ca²⁺, Co²⁺, Mg²⁺, Cd²⁺, Ba²⁺, Na⁺, K⁺, Mn²⁺, Fe²⁺, Pb²⁺, Ni²⁺, Pd²⁺, Hg²⁺ and after adding 10μL different biomolecules (B) Human Hemoglobin, Mayoglobin, Pepsin, BSA, Cytochrome-C.

Table S1 Stability of pSTEC₄-AgNPs assembly at different pH conditions

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<td>Stability of pSTEC₄-AgNPs</td>
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**Fig.S4** ESI-MS spectra of the mixtures of (A) pSTE_{4}-AgNPs(B) pSTE_{4}-AgNPs-Fe^{3+}.

Reference: