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General Information. All reactions were carried out under nitrogen; all solvents were freshly distilled under nitrogen and stored over molecular sieves for at least 3h prior to use. All other reagents were of reagent grade quality as obtained from commercial suppliers and were used without further purification. Column chromatography were performed on silica gel 63-200 mesh. NMR spectra were recorded in CDCl₃ unless otherwise indicated.


General procedure: a mixture of calix[4]arene 1 (3.0 g, 7.0 mmol), K₂CO₃ (2.9 g, 21.0 mmol), KI (catalytic) and the appropriate tosylate 2a,b (21.0 mmol) in CH₃CN (150 ml) was stirred and heated under reflux for five days. The solvent was then evaporated under vacuum and the residue taken up with CH₂Cl₂. The organic phase was washed with water 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 9 : ethyl acetate 1).

Compound 3a is a known compound, the spectral data are in agreement to those found in the literature:¹ MS(Cl) (m/z): 589 (MH⁺). m.p.: 110-111 °C.

Compound 3b: yellowish solid (65% yield); ¹H NMR (CDCl₃, 300 MHz, ppm): δ 1.34-1.48(20H, m), 1.67-1.72(4H, m), 2.01-2.09(8H, m), 3.37(4H, J=14 Hz, d), 3.99(4H, J=14 Hz, t), 4.32(4H, J=14 Hz, d), 4.91-5.02(4H, m), 5.75-5.85(2H, m),
6.64(2H, J=7 Hz, t), 6.73(2H, J=7 Hz, t), 6.91(4H, J=7 Hz, d), 7.04(4H, J=7 Hz, d), 8.17(2H, s). $^{13}$C NMR (CDCl$_3$, 75 MHz, ppm): δ 24.8, 27.9, 28.3, 28.4, 28.8, 30.2, 32.6, 76.4, 112.9, 117.7, 124.0, 127.0, 127.2, 127.6, 132.3, 138.0, 150.8, 152.2.

MS(CI) (m/z): 729 (MH$^+$) m.p.: 120-121 °C. Elemental analysis for C$_{50}$H$_{64}$O$_4$: calcd. C: 82.37%, H: 8.85%; found C: 82.65%, H: 9.10%.


General procedure: compound 3a or 3b (4.2 mmol) and thioacetic acid (1.3 g, 17.0 mmol) were dissolved in toluene (100 ml). The solution was fluxed with argon for 30 min., then AIBN (catalytic) was added and the resulting mixture was refluxed for further 3 h. The solvent was then evaporated under vacuum and the solid taken up with CH$_2$Cl$_2$. The organic phase was washed with water and with a solution of NaHCO$_3$, dried over anhydrous Na$_2$SO$_4$ and evaporated to dryness. The solid residue was dissolved in ethanol (70 ml) and mixed with a saturated solution of CH$_3$ONa in methanol. The greenish resulting heterogeneous mixture was stirred at room temperature for 24 h, then the solvent was evaporated under vacuum. The crude residue was taken up with CH$_2$Cl$_2$ and the organic phase washed with a 2N solution of HCl and then water up to neutrality and evaporated to dryness.

Compound 4a: purification of the residue by recrystallization with ethanol gave 4a as a white solid (80% yield): $^1$H NMR (CDCl$_3$, 300 MHz, ppm): δ 1.66-1.77(14H, m), 2.08-2.10(4H, m), 2.76(4H, J=7 Hz, t), 3.38(4H, J=14 Hz, d) 3.98(4H, J=7 Hz, t), 4.31(4H, J=14 Hz, d), 6.64(2H, J=7 Hz, t), 6.73(2H, J=7 Hz, t), 6.90(4H, J=7 Hz, d), 7.05(4H, J=7 Hz, d), 8.18(2H, s). $^{13}$C NMR (CDCl$_3$, 75 MHz, ppm): δ 25.7, 28.9, 29.04, 30.0, 31.4, 31.6, 37.3, 118.9, 125.2, 128.1, 128.4, 128.8, 133.3. MS (m/z): 656(M$^+$). m.p.: 139-140 °C. Elemental analysis for C$_{40}$H$_{48}$O$_4$ S$_2$: calcd. C: 73.13%, H: 7.36%, S: 9.76%; found C: 73.30%, H: 7.60%, S: 10.10%.

Compound 4b: purification of the residue by recrystallization with ethanol gave 4b as a white solid (60% yield): $^1$H NMR (CDCl$_3$, 300 MHz, ppm): δ 1.08-1.30(22H, m),
1.48-1.59 (8H, m), 1.88-1.95 (8H, m), 2.54 (4H, t), 3.23 (4H, J=14 Hz, d), 3.83 (4H, t), 4.12 (4H, J=14 Hz, d), 6.47 (2H, J=7 Hz, t), 6.62 (2H, J=7 Hz, t), 6.82 (4H, J=7 Hz, d), 6.91 (4H, J=7 Hz, d), 8.19 (2H, s). ^13C NMR (CDCl₃, 75 MHz, ppm): δ 25.9, 26.1, 28.5, 29.0, 29.1, 29.5, 29.7, 29.9, 30.1, 31.3, 31.4, 118.9, 125.2, 128.1, 128.3, 128.8, 133.4, 153.3. EI-MS (m/z): 818 (MNa⁺). m.p.: 300-302°C. Elemental analysis for C₅₀H₆₈O₄S₂: calcd. C: 75.33%, H: 8.60%, S: 8.05%; found C: 75.40%, H: 8.85%, S: 8.34%.

Preparation of nanoparticles stabilised with dodecanethiol: 50 ml of an aqueous solution of hydrogen tetrachloroaurate (0.2 g, 0.5 mmol) was mixed with a solution of tetraoctyl ammonium bromide (0.8 g, 1.5 mmol) in 100 ml of toluene at room temperature. The two-phase mixture was vigorous stirred until all the tetrachloroaurate was transferred in the organic layer. \( n \)-dodecanethiol (0.3 g, 1.5 mmol) was then added to the organic phase and 20 ml of an aqueous solution of NaBH\(_4\) (0.4 g, 10 mmol) was added under vigorous stirring. After 3 h, the organic phase was separated and the solvent was evaporated under vacuum. Methanol was added and the mixture was kept for 1 h at \(-20^\circ\)C. A dark precipitate of the nanoparticles formed upon standing which was filtered off, washed with few portions of methanol, dried under high vacuum and stored under argon at \(-20^\circ\)C. Yield 90%.

General procedure for the preparation of nanoparticles N1-6: dodecanethiol-stabilised nanoparticles (50 mg), prepared as described in the previous step, were mixed in toluene at room temperature with different percentage of the appropriate receptor (4a or 4b) for 5 days. The resulting mixture was purified by column chromatography (silica gel, \( n \)-hexane : ethyl acetate = 4 : 1), followed by ultracentrifugation of the eluate.

N1, exchange: 15% (75 mg of 4a used during the preparation);
N2, exchange: 75% (375 mg of 4a used during the preparation);
N3, exchange: 100% (500 mg of 4a used during the preparation).
Elemental analysis: Au 60%-Organic 40%.

N4, exchange: 10% (70 mg of 4b used during the preparation);
N5, exchange: 50% (350 mg of 4b used during the preparation);
N6, exchange: 100% (700 mg of 4b used during the preparation).
Elemental analysis: Au 55%-Organic 45%.
$^1$H NMR of nanoparticle N3 in CDCl$_3$ (300 MHz).
$^1$H NMR of nanoparticle N6 in CDCl$_3$ (300 MHz).
Binding isotherms for the titration of tetramethylammonium tosylate with nanoparticle N6 in CDCl₃.

Job’s plot for the titration of N-methylpyridinium tosylate with nanoparticle N3 in CDCl₃.