

A ultrasensitive and specific detection of dimethoate using *p*-sulphonato calix[4]resorcinarene functionalized silver nanoprobe in aqueous solution

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1. Experimental

1.1 Materials and methods

All chemicals used were of analytical grade or of the highest purity available. All solutions were prepared with double-distilled and deionized water. AgNO₃ (crystal extra pure) was purchased from Merck. All the pesticides were purchased from the Gujarat agro industries corporation limited. All pesticides standards were of 99% purity and were dissolved in deionized water. Sodium citrate were obtained from Thomas Baker. All other solvents used were of analytical grade. Deionized and doubly distilled water was used throughout the study. The morphology and size of the nanoparticles were estimated using the Transmission Electron Microscope (TEM). The particle size distribution was studied using Dynamic Light Scattering (DLS) (Nanotracs NPA150/250). UV–Vis absorption spectra were acquired on a Jasco V-570 UV–vis spectrometer. IR spectra were measured with a Bruker Tensor 27 FT-IR spectrometer.

1.2 Microwave synthesis of silver nanoparticles:

The procedure was essentially the same as those developed by Menon et al¹ with difference only in the use of microwave for the synthesis. The molar ratio of AgNO₃ 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 0.20 mM AgNO₃ solution and 2 ml of 10 mM sodium citrate and was heated at 80 °C at a power up to 150 W for 4 min. The solution changed from pale yellow to burgundy to yield Ag nanoparticles of 38±5 nm.

1.3 Synthesis of calix[4]resorcinarene

To a solution of resorcinol 1 (10 mmol) and aldehydes 2 (10 mmol) was added a solution of 2-ethoxyethanol (2 mL) and concentrated HCl (2 mL). This mixture was heated by microwaves for 3 min with a fixed power of 100 W. Resulted crude product was crystalized with absolute ethanol to get fine orange crystal. **Elemental analysis** calculated for C₃₆H₄₈O₁₂ %C 73.67, %H 5.30 found %C 73.52 %H 5.24. **¹H NMR** (400 MHz, CDCl₃, Me₄Si): δ 9.52 (s, 8H, Ar-OH), 6.82-7.43 (s, 24H, Ar-H), 4.18 (s, 4H, bridge –CH), 2.12 (s, 12H, –OCH₃). **FT-IR** (KBr) ν: 3278 cm⁻¹ (–OH), 2989 cm⁻¹ (Ar-CH). **ESI-MS** observed m/z 913.22 (M+1).

1.4 Synthesis of sulphonated calix[4]resorcinarene

A mixture of calix[4]resorcinarene (5.44 g, 0.01 mol), a solution of 37% formaldehyde (4.1 g, 0.05 mol) and sodium sulfite (6.3 g, 0.05 mol) in distilled water (50 ml) was stirred and heated at 90-95°C for 4 h, dilute hydrochloric acid (2 N) was added after cooling to adjust the pH to 7, followed by acetone (150 ml) to precipitate the product. The solid was filtered, washed with acetone (25 ml) and dried to get sulphonated calix[4]resorcinarene. **Elemental analysis** calculated for $C_{56}H_{44}O_{24}S_4Na_4$ %C 50.83, %H 3.32 found %C 50.72 %H 3.24. **1H NMR** (400 MHz, $CDCl_3$, Me_4Si): δ 10.42 (s, 8H, Ar-OH), 7.5 (s, 20H, Ar-H), 4.18 (s, 4H, bridge-CH), 2.12 (s, 12H, $-OCH_3$), **^{13}C NMR** (125 MHz, $CDCl_3$, Me_4Si): 13, 13.6, 14, 15.3, 23, 28, 30, 32, 39.51, 123.66, 126.0, 140, 160, 162, 164 (Ar-C). **FT-IR** (KBr) ν : 3278 cm^{-1} (-OH), 2989 cm^{-1} (Ar-CH). **ESI-MS** observed m/z 1322 (M^+).

1.5 Preparation of pSC₄R capped silver nanoparticles (pSC₄R-AgNPs):

5 ml of 0.20 mM silver nanoparticles was added to 5 ml 0.10 mM *p*-sulphonated calix[4]resorcinarene(pSC₄R) and kept stirring for 1 h. Then, 0.15 mM *p*-sulphonated calix[4]resorcinarene(pSC₄R)capped silver nanoparticles(pSC₄R-AgNPs) was obtained.

1.6 Dimethoate detection using pSC₄R-AgNPs

The stock solution of dimethoate (0.01 M) was prepared by dissolving dimethoate (2.29 g) in deionised water. Further, it was diluted to the range of 1.0×10^{-9} , 2×10^{-9} , 3.0×10^{-9} , 5×10^{-9} , 7.0×10^{-9} , 10×10^{-9} and detected by 0.15 mM *p*-sulphonated calix[4]resorcinarene(pSC₄R)capped silver nanoparticles(pSC₄R-AgNPs). To detect dimethoate, 2 ml of 0.1 mM dimethoate was added into 3 ml of pSC₄R-AgNPs with 2 ml of phosphate buffer pH-5 and made up to 10 ml. The shift in the SPR absorption maxima of the pSC₄R-AgNPs on adding predetermined quantities of dimethoate standard is recorded using a UV-Visible absorption spectrophotometer and a calibration curve was plotted.

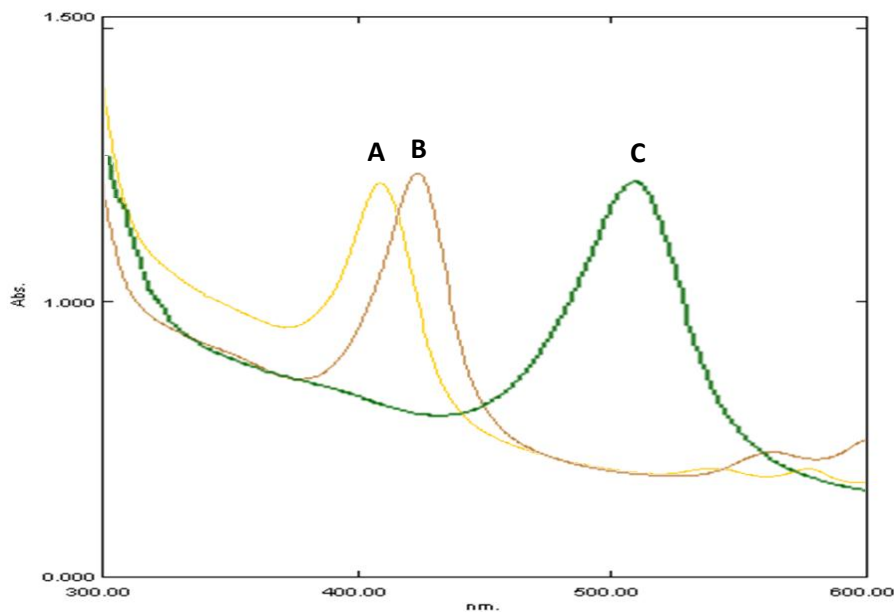


Fig.S1 The UV-Vis spectra of (A)Pure AgNPs, (B)pSC₄R-AgNPs and (C)dimethoate-pSC₄R-AgNPs.

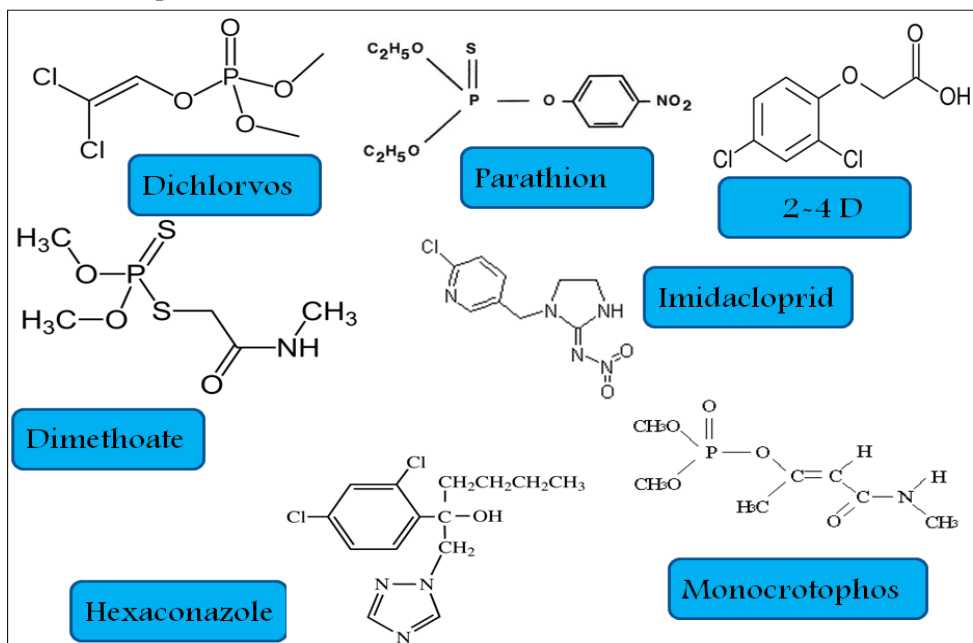
pH	2	4	6	8	10
Stability of pSC₄R-Ag NPs	7 h	9 h	Weeks	Months	Months

Table S1 Stability of pSC₄R- AgNp assembly at different pH conditions

Sample	Added(10⁻⁸ M)	Found(10⁻⁸M)	Recovery (%)	RSD (%) (n-3)
Industrial Waste water	0	18	–	1.10
	10	26	97.2	0.92
	20	34	96.8	1.32
	50	66	97.1	1.12

Table S2 shows the results of determination of dimethoate in industrial waste water

1.7 Structure of other pesticide:



References:

1. A. Pandya, K.V. Joshi, N.R. Modi, S. K. Menon, *Sensors and Actuators*, 2012, **168**, 54– 61.