Emerging Trends Based on Calix Protected Metal Nanoparticles

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ABSTRACT

Metal nanoparticles are of extreme interest because of the new properties (such as chemical reactivity and optical behavior) they exhibit compared with larger particles. Calixarenes and their hydrazide derivative, are large bulkier macrocycles with web type structure and inherent hollow cavity, acts as reducing agent as well as encapsulates the nanoparticles and yields stable water dispersible nanoparticles. In this context, we have synthesized calix-protected metal nanoparticles, such as calix-nanogold, calix-nanosilver, calix-nanopalladium, calix-nanoalloy of gold and silver, using different calix hydrazide systems. Moreover, exciting and fascinating applications of the prepared calix-nano hybrids as selective and sensitive sensors for metal ions and amino acids, as catalysts for organic chemical reactions: Suzuki, Heck, Sonogashira and Stille reactions have been carried out. The metal nanoparticles, found to be good antimicrobial agent and can form a future basis for their potential use in new pharmaceutical formulations, as well as biosciences, chemical sciences and other area of research.

Keywords*: *calixarenes; supramolecule; chemistry; metal nanoparticles

INTRODUCTION

After crown ethers and cyclodextrins, calixarenes are classified as third generation supramolecules. The term "calixarenes" was coined by Prof. C.D. Gutsche in 1978. Calixarenes are cyclic phenolic compound and are the condensation product of phenol and aldehyde [1]. In addition to basic calixarenes, resorcinarenes, calixpyrroles, thiacalixarenes and oxacalixarenes have also gained lot of importance due to their versatile nature [2-5] **Figure 1**. Nanoparticles are special and fascinating entities with dimensions ranging from 1-100 nm. The smaller size and increased surface area makes these nanoscale materials posess unique physical and chemical characteristics that are substantially different from bulk materials and thereby find applications in materials science, analytical chemistry, biochemistry, catalysis, medicine, nanoelectronics [6-8]. Calixarenes chemistry has contributed a lot in the field of nanoscience and inter-related research. It has been reviewed as "Conjugates of calixarenes emerging as molecular entities of nanoscience" [9], "Gold nanoparticles functionalized with supramolecular macrocycles" [10] and

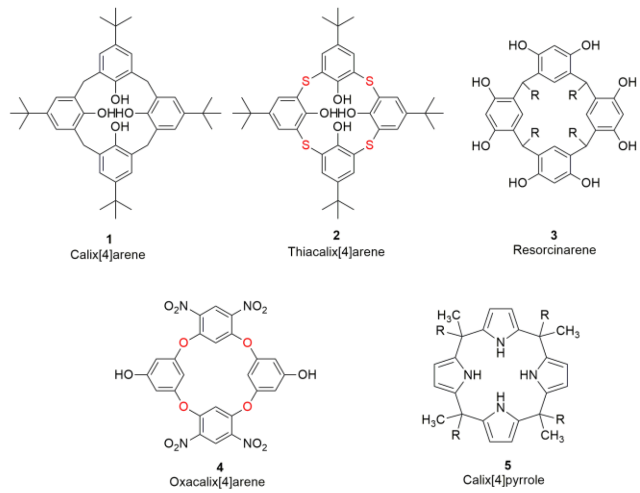


Figure 1 Schematic structures 1-5 of different calix platforms

"Metal nanoparticles and supramolecular macrocycles: A tale of synergy" [11].

In this article synthesis of stable and water dispersible calix protected metal nanoparicles (Au, Ag, Pd etc.) by simple one pot method is reported. Attempt is being made to discuss the synthesis, characterisation, mechanism of intercation and applications of the synthesised nanoparticles in the area of sensing (biomolecules, cations, pesticides and stimulants for warfare agents) by spectrophotomotery and spectrofluorimetry. In addition, their use as antimicrobial agent, as random access memory device, molecular logic gate and as an antioxidant will also be discussed.

SYNTHESIS

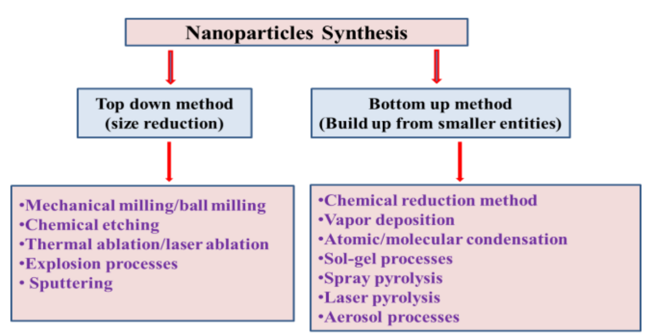
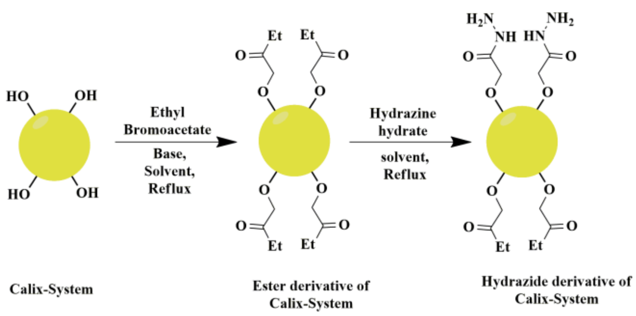


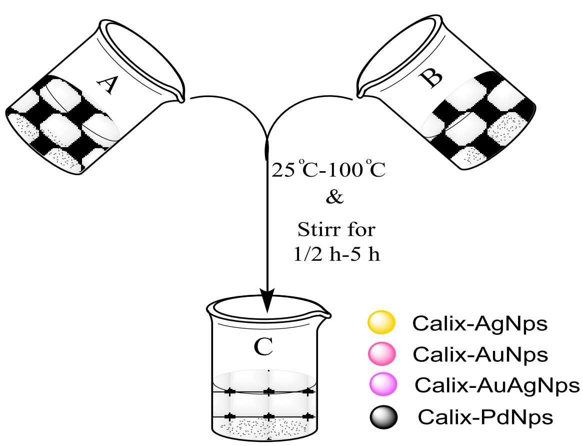
Figure 2 various method to synthesize metal nanoparticles

There are two methods (**Figure 2**) by which we can synthesise metal nanoparticles. Out of the two, bottom up method is better beacause of its ease and out of various such methods, chemical reduction method is considered best to yield comparativlely stable metal nanoparticles. The stability of such produced metal nanoparticles can be further enhanced if we prevent them from agglomeration by using some capping agent. Here comes hydazide derivative of any of the calix platform (1-5) mentioned in **Figure 1**. to our rescue, which can be prepared as per **Scheme 1.**



Scheme 1 Graphical representation for the synthesis of hydrazide derivative of calix-system

All the calix systems have been well characterised by various spectroscopic techniques. Using these water soluble hydrazide derivative of various calix platforms/system the water dispersible metal nanopericles are prepared as per **Scheme 2**. The temperature and raection time varies for different system.



A = Water soluble hydrazide of calix-system
B = Water soluble metal salts of Au,Ag and Pd
C = Water dispercible calix protected MNps

Scheme 2 Graphical representation of preparation of water dispersible metal nanoparticles

The fetures of calix based metal nanoparticles depends on the reducing ability of the number of hydrazide groups attached on calixarene moiety and stabilizing ability of the web-type structure of parent calix platform. To prepare stable metal nanoparticles hydrazide derivative of calixplatform should effectively engulf and passivate the surface of the metal atoms. My research group have synthesized different calix hydrazides [12-15] (**Scheme 2)** which reduces the metal ions by the transfer of electrons from amine groups to metal ions and also acts as a strong capping agent. Lone pair of nitrogen of the $–NHNH_2$ coordinates/binds with the metal on the outside of the nanoparticles. No sign of precipitation or aggregation was observed of the prepared nanoparticles for quiet a long time.

The reduction method to prepare nanoparticles using hydrazine hydrate is depicted in an equation 1 by Shen et al. [16] in their work for preparing gold nanoparticles (AuNps):

$$4HAuCl_4 + 3N_2H_5OH \rightarrow 4Au + 16HCl + 3N_2 + 3H_2O \quad (1)$$

The chemistry behind how calix engulfs the metal nanoparticles in its hollow and stabilize the metal nanoparticles for long period of time is yet to be explored further. Some understanding on the mechanism of interactions of calix system with metal nanoparticles are discussed by Ha et al. [17].

APPLICATIONS

We have used well characterised calixpoyydrazide (CPH), octamethoxy resorcinarene tetrahydrazide (OMRTH), resorcinol calixpyrrole octahydrazide (RCPOH), calixresorcinarene tetrahydrazide (CRTH) and thiacalix tetrahydrazide (TCTH) for the formation of silver nanoparticles (AgNps). Results of CPH-AgNps as selective turn off sensor for Fe^{3+} ions [18] , OMRTH-AgNps as turn off sensor for Cd^{2+} ions[13], CPOH-AgNps as turn on sensor for Hg^{2+} ions[19], CRTH-AgNps as turn off sensor for Pb^{2+} ions and TCTH-AgNps as turn off sensor for tryptophan as well as turn on sensor for histidine[20]. All the properties and parameters are mentioned in **Table 1**.

Moreover, these calix platforms i.e. CPH, OMRTH, RCPOH, CRTH, TCTH have also been used to prepare Gold nanoparticles (AuNps) and found to be selective and sensitive sensor for various metal ions and amino acids. For example, CPH-AuNps as turn off sensor for Hg^{2+} ions and dopamine[15], OMRTH-AuNps as turn off sensor for Cu^{2+} ions and turn on sensor for leucine, CPOH-AuNps as turn off sensor for Co^{2+} ions[21], CRTH-AuNps as turn off sensor for phenylalanine[22], and TCTH-AuNps as turn on sensor for isoleucine. All the properties and parameters are mentioned in **Table 2**.

Some of the calix protected Pd nano partcicles are being explored for their catalytic activity particularly in C-C coupling reactions [23], **Table 3**.

Calix protected metal nanoparticles can be considered as multifunctional nanoparticles for two reasons, one, their existence and another their application. Existence, as they have different functional groups exposed on their periphery and application, as they can perform different functions. In addition to the results already mentioned the other functions which are being worked out in our laboratory are their trial for drug delivery vehicle as they show interaction with CT-DNA and S-DNA. Their use as molecular logic gate to generate sequential information processing device for two chemical inputs and use as

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random access memory device as few calix protected metal nanoparticles show characteristic current voltage path which is sure signature of theirs possessing some memory element. Since preliminary screening shows that most of the calix protected metal nanoparticles exhibit reasonably good antimicrobial activity therefore efforts are being made to explore their commercial potential. Likewise getting antioxidant behaviour of calix protected nanoparticles comparable with standard quercetin and ascorbic acid has led us to further quantify the results.

Table 1 Details of Synthesized Calix protected AgNps

Parameters		CPH	OMRTH	CPOH	CRTH	TCTH
		AgNps				
System		Aqueous				
Colour		yellow	yellow	yellow	Yellowish orange	yellow
SPR (λ max) nm		408	410	427	426	425
Re-dispersed SPR (λ max)		415	410	430	427	424
Zeta potential		21	12	14	14.3 ±2	21
Emission (λEm)		560	450	580	531	579
Stability	Days	120	180	120	90	90
	Temp(^{0}C)	30-40	30	20-30	20-30	10-40
	pH (4-10)	7	7	6	7	5-9
Size	PSA	120	132	112	126	119
	TEM	5	5-10	5-8	15±5	20±2
sensor	Cations	Fe^{3+}	Cd^{2+}	Hg^{2+}	Pb^{2+}	-
	Anions	-	-	-	-	-
	Amino acid	-	-	-	-	Tryptophan Histidine
	DNA Intera-ction	-	-	-	Weak	Weak
Ref.		[18]	[13]	[19]		[20]

Table 2 Details of Synthesized Calix protected AuNps

Parameters		CPH	OMRTH	CPOH	CRTH	TCTH
		AuNps				
System		Aqueous				
Colour		ruby red	purple	red-purple	ruby red	ruby red
SPR (λ max) nm		530	545	535	527	538
Re-dispersed SPR (λ max)		532	550	540	529	540
Zeta potential		18	19	14	10.7	24
Emission (λEm)		660	560	620	540	637
Stability	Days	90	180	120	120	90
	Temp (^{0}C)	0-10	0-20	30-40	10-40	10-40
	pH (4-10)	4-10 pH	4-10 pH	5-9 pH	4-10 pH	4-10 pH
Size	PSA	120	132	112	126	119
	TEM	5	10±2	8±2	11±2	10±2
Sensor	Cations	Hg^{2+}	Cu^{2+}	Co^{2+}	-	-
	Anions	-	-	-	-	-
	Amino acid	Dopamine	Leucine	-	Phenylalanine	Isoleucine
	DNA Intera-ction	Weak	Weak	Strong	Weak	Strong
Ref.		[15]		[21]	[22]	

Table 3 Details of Synthesized Calix protected PdNps

Parameters		CPTH	TMRTH	DHOC
		PdNPs		
System		Aqueous		
Colour		Colloidal black	Colloidal black	brownish black
Zeta potential		-28.4	-16.4	-28.9
Stability	Days	60 days	60 days	60 days
Size	TEM	5±2	5±2	5±2
Application	Catalytic activity	Heck reaction	Suzuki reaction	Suzuki, Heck and Sonogashira

CONCLUSION

We have successfully synthesised few water soluble calix systems which have been used for one pot synthesis of water dispersible stable Au, Ag and Pd multifunctional nanoparticles. They have been found to function as selective and sensitive fluorescent Turn-on and Turn-off sensors for various metal ions and amino acids. Due to appropriate size (5-18 nm) and very high stability (more than six months) of these water dispersible multifunctional nanoparticles they hold great potential and herald many promises for their application in biosciences, chemical sciences and other area of research. The quest which needs to be addressed that what is that which makes these calix protected metal nanoparticles to show selectivity for a particular analyte. It is neither the organic moiety i.e. calix hydrazide nor the individual metal nanoparticles. It has to be a combination of both. Therefore it is very much essential to know how calix is bound to nanoparticles and what remains on its surface for showing their selective behaviour.

REFERENCES

[1] C.D. Gutsche, Calixarenes, Accounts of Chemical Research, 16 (1983) 161-170.

[2] R. Kumar, Y.O. Lee, V. Bhalla, M. Kumar, J.S. Kim, Recent developments of thiacalixarene based molecular motifs, Chemical Society reviews, 43 (2014) 4824-4870.

[3] V. Jain, P. Kanaiya, Chemistry of calix [4] resorcinarenes, Russian Chemical Reviews, 80 (2011) 75-102.

[4] V. Mehta, M. Panchal, K. Modi, A. Kongor, U. Panchal, V. K Jain, The Chemistry of Nascent Oxacalix [n] hetarene (n≥ 4): A Review, Current Organic Chemistry, 19 (2015) 1077-1096.

[5] V.K. Jain, H.C. Mandalia, The chemistry of calixpyrroles, Heterocycles, 71 (2007) 1261-1314.

[6] P. Herves, M. Pérez-Lorenzo, L.M. Liz-Marzán, J. Dzubiella, Y. Lu, M. Ballauff, Catalysis by metallic nanoparticles in aqueous solution: model reactions, Chemical Society Reviews, 41 (2012) 5577-5587.

[7] P. Taladriz-Blanco, P. Hervés, J. Pérez-Juste, Supported Pd Nanoparticles for Carbon–Carbon Coupling Reactions, Topics in Catalysis, 56 (2013) 1154-1170.

[8] R.A. Alvarez-Puebla, L.M. Liz-Marzán, SERS detection of small inorganic molecules and ions, Angewandte Chemie International Edition, 51 (2012) 11214-11223.

[9] A. Acharya, K. Samanta, C.P. Rao, Conjugates of calixarenes emerging as molecular entities of nanoscience, Coordination Chemistry Reviews, 256 (2012) 2096-2125.

[10] H. Li, Y.-W. Yang, Gold nanoparticles functionalized with supramolecular macrocycles, Chinese Chemical Letters, 24 (2013) 545-552.

[11] V. Montes-García, J. Pérez-Juste, I. Pastoriza-Santos, L.M. Liz-Marzán, Metal Nanoparticles and Supramolecular Macrocycles: A Tale of Synergy, Chemistry-A European Journal, 20 (2014) 10874-10883.

[12] K.D. Bhatt, D.J. Vyas, B.A. Makwana, S.M. Darjee, V.K. Jain, Highly stable water dispersible calix[4]pyrrole octa-hydrazide protected gold nanoparticles as colorimetric and fluorometric chemosensors for selective signaling of Co(II) ions, Spectrochimica acta. Part A, Molecular and biomolecular spectroscopy, 121 (2014) 94-100.

[13] B.A. Makwana, D.J. Vyas, K.D. Bhatt, S. Darji, V.K. Jain, Novel fluorescent silver nanoparticles: sensitive and selective turn off sensor for cadmium ions, Applied Nanoscience, (2015) 1-12.

[14] D.R. Mishra, S.M. Darjee, K.D. Bhatt, K.M. Modi, V.K. Jain, Calix protected gold nanobeacon as turn-off fluorescent sensor for phenylalanine, Journal of inclusion phenomena and macrocyclic chemistry, (2015) 1-12.

[15] D.J. Vyas, B.A. Makwana, H.S. Gupte, K.D. Bhatt, V.K. Jain, An efficient one pot synthesis of water-dispersible calix [4] arene polyhydrazide protected gold nanoparticles-A “turn off” fluorescent sensor for Hg [II] ions, Journal of nanoscience and nanotechnology, 12 (2012) 3781-3787.

[16] M. Shen, W.-f. Chen, Y. Sun, C.-g. Yan, Synthesis and characterization of water-soluble gold colloids stabilized with aminoresorcinarene, Journal of Physics and Chemistry of Solids, 68 (2007) 2252-2261.

[17] J.-M. Ha, A. Katz, A.B. Drapailo, V.I. Kalchenko, Mercaptocalixarene-Capped Gold Nanoparticles via Postsynthetic Modification and Direct Synthesis: Effect of Calixarene Cavity-Metal Interactions, The Journal of Physical Chemistry C, 113 (2008) 1137-1142.

[18] B.A. Makwana, D.J. Vyas, K.D. Bhatt, V.K. Jain, Y.K. Agrawal, Highly stable antibacterial silver nanoparticles as selective fluorescent sensor for Fe 3+ ions, Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, 134 (2015) 73-80.

[19] K.D. Bhatt, D.J. Vyas, B.A. Makwana, S.M. Darjee, V.K. Jain, H. Shah, Turn-onfluorescenceprobe for selective detection of Hg (II) by Calixpyrrole hydrazide reduced silver nanoparticle: Application to real water sample, Chinese Chemical Letters, (2016).

[20] S.M. Darjee, K.D. Bhatt, U.S. Panchal, V.K. Jain, Scrupulous recognition of biologically important acids by fluorescent “turn off–on” mechanism of thaicalix reduced silver nanoparticles, Sensing and Bio-Sensing Research, (2016).

[21] K.D. Bhatt, D.J. Vyas, B.A. Makwana, S.M. Darjee, V.K. Jain, Highly stable water dispersible calix [4] pyrrole octa-hydrazide protected gold nanoparticles as colorimetric and fluorometric chemosensors for selective signaling of Co (II) ions, Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, 121 (2014) 94-100.

[22] D.R. Mishra, S.M. Darjee, K.D. Bhatt, K.M. Modi, V.K. Jain, Calix protected gold nanobeacon as turn-off fluorescent sensor for phenylalanine, Journal of Inclusion Phenomena and Macrocyclic Chemistry, 82 (2015) 425-436.

[23] U. Panchal, K. Modi, M. Panchal, V. Mehta, V.K. Jain, Catalytic activity of recyclable resorcinarene-protected antibacterial Pd nanoparticles in CC coupling reactions, Chinese Journal of Catalysis, 37 (2016) 250-257.