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GRAPHICAL ABSTRACT

Seven gelator molecules, which gave supramolecular gels, produced gold nanoparticles and fluorescent small gold nanoclusters.. The AuNPS embedded gels can, catalyze the reductionof p-nitrophenol to p-aminophenol without use of any external reducing agent. The fluorescent gold nanoclusters act as the sensor for Hg(II) by their fluorescence quenching.

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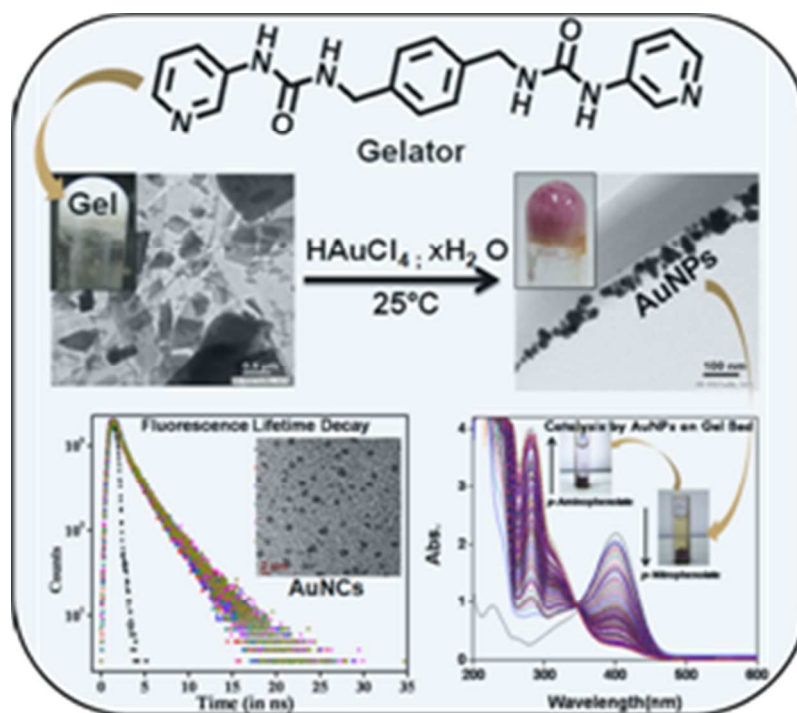
ARTICLE

Synthesis of Gold Nanoparticles and Nanoclusters in Supramolecular Gel and Their Applications in Catalytic Reduction of *p*-Nitrophenol to *p*-Aminophenol and Hg (II) Sensing

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A new series of urea/amide functionalized bis-pyridyl compounds were found to give gels in various solvent systems, viz. DMF/water, DMSO/water, Ethylene Glycol/water and nitrobenzene. On sprinkling solid $HAuCl_4; xH_2O$, in these gel, small gold nano-clusters/ gold nano-particles (AuNCs/AuNPs) were found to form; without use of any exogenous reducing agent. The AuNPs embedded gels were capable of catalyzing the reduction of *p*-Nitrophenol to *p*-Aminophenol and that too without any external reducing agent like $NaBH_4$. The small gold nanoclustes formed in the nitrobenzene gel of the gelators were fluorescent and this property has been exploited for sensing of Hg (II).

1. Introduction

Supramolecular gels (SGs) are an important class of visco-elastic materials because of their various potential applications in materials science, technology and catalysis.[1-9] When a homogeneous solution of a small gelator molecule having molecular weight typically below 3000 – popularly known as low molecular weight gelators (LMWGs) – is allowed to settle down often after a brief exposure to external stimuli (viz. heat, sound, pH modulation etc.), the whole volume of the solution becomes a solid-like mass that can withstand its own weight against gravitation; such solid-like mass is known as supramolecular gel. Inside the gel, the gelator molecules self-assemble themselves via various supramolecular interactions such as hydrogen bonding, π-π stacking, van der Waals interactions, hydrophobic interactions etc. to produce a supramolecular network (gel network often known as self-assembled fibrilar networks or SAFiNs)[10] within which the solvent molecules are trapped or immobilized. Among the various applications that SG offers, developing different nano-structures by exploiting gel network as template is a matter of great challenge as gaining control over the intriguing morphologies of the nano-structures is difficult and important in the context of technological applications. [11-14]

Compared to the bulk metals, metal nanoparticles (MNPs) display unique physical and chemical properties[15-17] and in recent years, SGs are being used as template on which MNPs are generated.[18] There are three ways MNPs can be generated/ stabilized on gel-network: a) MNP is generated in a separate experiment and allowed to get absorbed on gel-network, b) MNPs are generated on SG using exogenous reducing agent and c) MNP is generated on SG itself wherein the gel-network acts as both template, reducing and stabilizing

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agent. Although there are quite a few examples belonging to the first two categories, [19-27] *in situ* synthesis of MNP on SG without use of external reducing agent is technologically more advantegeous.[28-38] A subclass amidst the metal nanoparticles is small metal nanoclusters (MNCs), where the size regimen of metal nanoparticles is 2 nm or less and they have electrical, optical, magnetic and catalytic properties which are quite different from large metal nanoparticles (3nm-50nm). Study on small noble metal nanoclusters is a very promising and interesting topic which generates wide range of attention nowadays.[39-48] The AuNCs typically consist of several to tens of atoms and their sizes are comparable to Fermi wavelength of electrons.[49,50] As a result these AuNCs exhibit molecule like properties of discrete electronic states and can display size dependent photoluminescence ranging from UV-Vis to near-IR region, depending on the number of Au atoms in the clusters.[51,52]

In this report, we explored a series of disubstituted urea compounds as potential gelators for synthesizing AuNPs/AuNCs. We particularly selected bis-urea derivatives in order to ensure the formation of 1D hydrogen bonded network sustained by urea…urea hydrogen bonding that might impart gelation.[53] Secondly and more importantly; urea is a reducing entity, which can reduce Au^{3+} and subsequently produce and stabilize AuNPs (Au^{0}) . All the compounds in the series showed gelation ability with DMF/water, DMSO/water , Ethylene Glycol(EG)/water and nitrobenzene and AuNPs could be generated using these gels as template. Interestingly, no external stimuli, like heat or light, nor any pH modulation was required for the formation of the AuNPs or the AuNCs in the gel. Remarkably, the AuNPs embedded gels were capable of reducing *p*-Nitrophenol to *p*-Aminophenol at room temperature in catalytic fashion without use of any reducing agent like $NaBH_4$. To our knowledge, this is the first report of SG generated AuNPs capable of reducing a $-NO_2$ group to $-NH_2$ without using any external reducing agent. Another interesting aspect is, in nitrobenzene solvent, only small and stable Au nanoclusters (AuNCs of size range 2 nm or less), instead of AuNPs, were produced on the gel bed, which gave strong fluorescence. The fluorescence phenomenon of small AuNCs have been recognized for some time, and they have been used for many purposes including bio-imaging, cancer-therapy, sensing etc.[54-59] But example of formation of fluorescence AuNCs on supramolecular gel, is rare.[60] Herein we are also reporting the efficient Hg(II) sensing property of the AuNCs generated on the gel. Upon addition of the

aqueous solution of $HgCl_2$ the fluorescence intensity of the AuNCs was quenched immediately and to a significant extent.

2 Experimental

Materials
Among the chemicals used, particularly, dichloromethane (DCM, E Merck (GR), India) was distilled over CaH_2. Other chemicals namely, triphosgene, 3-Aminopyridine, p-Xylenediamine, 1,4-Diaminobutane,1,3-Diaminopropane, Ethylenediamine, Aniline, Ethylene Glycol (EG), DMF, DMSO, were procured commercially (ALDRICH/ E. Merck, India) and used without further purification. Millipore water (resistivity 18.2 $M\Omega.cm$), was used all through the experiments.

Characterizations
Microanalyses were performed on a Perkin-Elmer 2400 Series II elemental analyzer. UV-Vis spectra were recorded in a VARIAN CARY 100 Bio-spectrophotometer. FTIR spectra were recorded in a FTIR 8300 (Shimadzu) spectrophotometer. NMR was recorded in a BRUKER AVANCE III 500 spectrophotometer. Mass spectra were recorded in a Q-TOF micro mass spectrometer (WATERS). TEM photographs were taken in JEOL JEM 2010 microscope. Fluorescence measurements were performed with a Horiba Jobin Yvon Fluoromax-4 spectrofluorometer. Fluorescence lifetime decay measurements were done on Horiba–Jobin–Yvon FluoroCube fluorescence lifetime system using NanoLED at 450 nm (IBH UK) as the excitation source and TBX photon detection module as the detector. The decays are analyzed using IBH DAS-6 decay analysis software. The instrumental response time for our set up is approx.1 ns. Goodness of fits is evaluated from χ^2 criterion and visual inspection of the residuals of the fitted function to the data. All of the experiments are performed at 25 °C temperature with air-equilibrated solutions. XPS spectrum was recorded on a Omicron Nanotechnology 0571 model instrument.
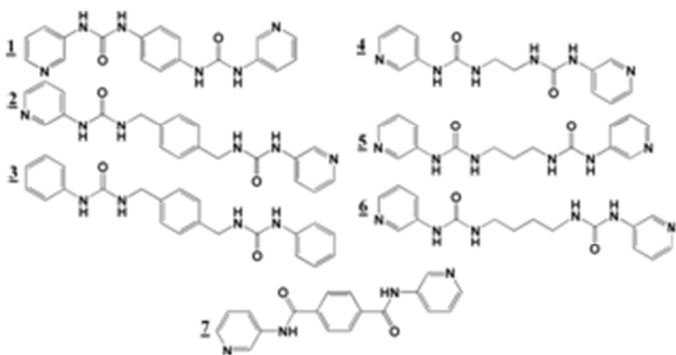
Synthesis
The bis-pyridyl-bis-urea derivatives **1-2**, **4-6** were synthesized by reacting the suitable diamine with 3-Aminopyridine following triphosgene protocol .The diphenyl analogue of **2** i.e. compound **3** was synthesized following the same procedure using aniline instead of 3-Aminopyridine. While compounds **2** and **3** are newly synthesized, the rests i.e. **1,4,5,6** and **7** were synthesized following reported protocol.[61-64] ^{1}H NMR spectra of **1-7** are provided in the ESI (Figs. S19- S25).

Synthesis of 2: Under inert (Ar) atmosphere, triphosgene (1.2g, 4.04mmol) was added to a solution of 3-Aminopyridine (1g, 10.6mmol) and triethylamine (3ml) in dichloromethane (DCM, 100ml) at 0°C and was stirred continuously with the help of a magnetic stirrer bar. A DCM solution (50ml) containing p-Xylenediamine (730mg, 5.35mmol) was added dropwise to the above solution at 0°C and stirring continued for another one hour at the same temperature. The stirring was allowed for 48 hours to obtain maximum yield of the product. After this, the product was filtered, thoroughly washed with DCM and dried. The dried product was then stirred with 5% $NaHCO_3$ for 3 hours and filtered. The mass obtained was meticulously washed with water until it became neutral as was indicated by a litmus paper. It was then dried in vacuo. Yield: 1.026 g, (2.72mmol, 25.6%). (Analytical data viz. elemental analysis, NMR, IR may be found in the ESI).

Synthesis of 3: Same as synthesis of **2**, except for aniline (677mg, 7.277mmol) in place of 3-Aminopyridine.Triphosgene used was 720mg, (2.425mmol) and triethylamine used was 2ml in dichloromethane at 0°C. Yield: 876 mg (2.341 mmol, 30.64 %).(Analytical data viz. elemental analysis, NMR, IR to be found in the ESI).

3 Results and discussion

Scheme 1 Gelator Molecules

Physical properties of the gel:
Total seven gelator molecules have been synthesized (Scheme 1). Compound **3** was particularly prepared in order to probe the role of pyridine moiety on gelation as well as AuNP formation. We had also synthesized a bis-pyridyl-bis-amide derivative **7** in order to study the role of amide moiety in AuNP formation. All the compounds **1-7** gave opaque gels (DMF/water,

DMSO/water, Ethylene Glycol (EG)/water, (1:5 v/v in all the cases) with minimum gelator concentration (MGC) of ~5 wt % (w/v)(except **4** and **5** which recorded MGC of ~10 wt % in DMF/water, DMSO/water and EG/water). All the gelators display high thermal stability (T_{gel} ~100° C).
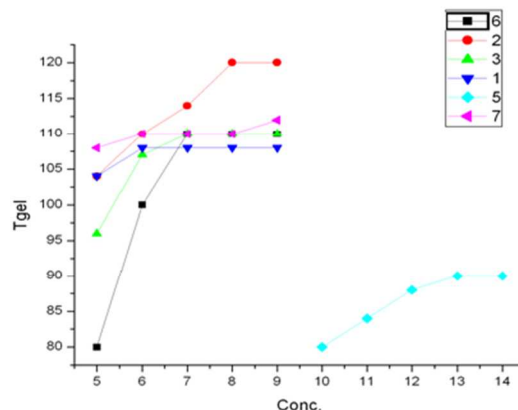

Fig. 1 T_{gel} vs. gelator concentration; all the gels were made from DMF/water (1:5 v/v). Different gelators are indicated in the legend.

To study the influence of supramolecular interactions on the thermal stability of the gels, we performed table top rheology by plotting T_{gel} vs. concentration of gelator as shown in Fig. 1.[65] T_{gel} steadily increased with the increase in gelator-concentration following a plateau indicating the involvement of various non-covalent supramolecular interactions such as hydrogen bonding, π-π stacking etc. in network formation. It appears from the plot that the gelators having aromatic backbone display higher thermal stability as compared to the gelators having aliphatic backbone.

While measuring the T_{gel}; the gel made of **5** behaved differently from that of the rest. Actually **5** (and also **4**) gave gel at 10% (w/v) (MGC), compared to other gelators which gave gel at 5% (w/v) (MGC) in DMF/water. So in the T_{gel} vs. concentration plot, **5** appeared differently from the rest (**1-3,6,7**). It may be observed that as we go down lower in the alkane chain length from **6** to **5** and **4** the MGC goes up. For **6** MGC was 5%, for **4** and **5** it was 10%. So the alkane chain length (actually the no. of C-H bonds in the alkane chain) has an important role in determining the MGC (with increase in the no. of C-H bonds the non-covalent interactions like C-H……π interaction, H bonding interaction etc. increases and this in turn helped in formation of the gel at lower MGC). For **4** we could not arrive at an reasonable T_{gel} vs. concentration plot because we

observed some inconsistency while determining the gel-melting temperatures of **4** at higher concentration of gels; resulting in a non-representable T_{gel} vs. concentration plot.

To study the morphology of the gel network, we performed high resolution transmission electron microscopy (HRTEM) of a selected gel. A fraction of 5 wt % gel (DMF/water 1:5 v/v) of **2** was scooped and carefully smeared on a carbon coated copper TEM grid and viewed under HRTEM at 200 KV. The gel network appears to constitute of ultra-thin discrete plates. Similar morphologies were also seen for a few other gels (viz. **6** and **7**) (Fig. 2, Fig. S1).

AuNP and AuNC syntheses and their characterization:

In a typical AuNP/AuNC formation experiment; $HAuCl_4.xH_2O$ (1-2 mg) and the corresponding gelator molecule (30 mg) were taken in 0.1 ml DMF and the resulting solution was heated strongly followed by the addition of 0.5 ml of water that produced orange precipitate instead of formation of gel. TEM observation of the mixture revealed the presence of Au nanoclusters (1-3 nm) (Fig. 3a). On the other hand, when the same above experiment was done but no water was added; an almost clear orange solution resulted, without any solid precipitate which showed the presence of highly-branched AuNPs (nanodendrites) in HRTEM (Fig. 3b and Fig. S9).[66-70] Interestingly, we got the same Au-nanodendrites formation on the supramolecular gel of **2** in DMF/water medium, (0.6 ml gel in DMF : water (0.1ml:0.5ml),if we sprinkle some solid powdered $HAuCl_4.xH_2O$ (1-2 mg) on the gel and keep it at room temperature , devoid of light. (Fig. S10).

Similarly, when an aqueous solution of the gold salt (1-2 mg gold salt dissolved in 2 ml water) was placed over the gel; AuNPs of similar kind were obtained inside the gel after 48 hours at room temperature (Fig. S3). TEM observation revealed the presence of AuNPs sticking to the surface of the gel fibers (Fig. 4 and Figs. 6a and 6b) and they were found to be arranged in a directional manner (Figs. 3b and 5a). The distribution of AuNPs were given in the histogram (Fig. 5b). In order to record UV-Vis absorption spectrum, the AuNPs were collected as suspension in EtOH and the corresponding UV-Vis spectrum recorded, which displayed the typical surface plasmon band (SPR) for AuNPs at 553 nm (Fig. 6c and Fig. S8). EDX of a selected area in HRTEM also revealed the presence of Au (Fig. S2). It may be noted that no external reducing agent like $NaBH_4$ had to be added for generation of the AuNPs , nor any external stimuli like heat or light or pH modulation was necessary. Remarkably, all the gelators **1-7** could thus

produce AuNPs. AuNPs could also be synthesized from the gels prepared from Ethylene Glycol (EG)/water or DMSO/water (1:5 v/v in both the cases) solvents. In all the cases the gel fibers stabilized the Au particles in the nanometer size regimen and the urea/amide moiety was supposed to be responsible for the necessary reduction of Au^{3+}.
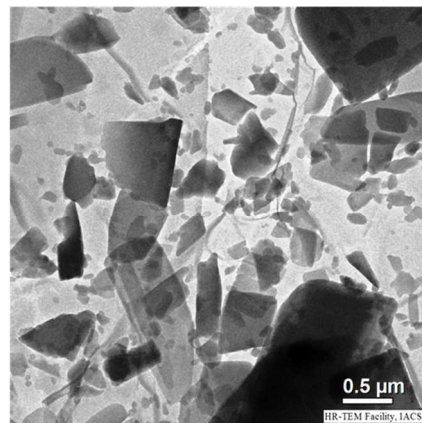

Fig.2 Ultra-thin plate like morphology of the gel network of **2** at MGC level in DMF/water (1:5, v/v), observed under HRTEM.
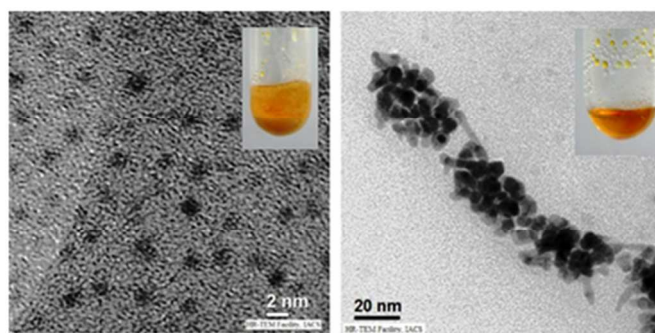

a)   b)

Fig. 3 a) HRTEM images of AuNCs and b) highly-branched nanodendrites of AuNPs; insets – orange precipitates and orange solution as described in the text.
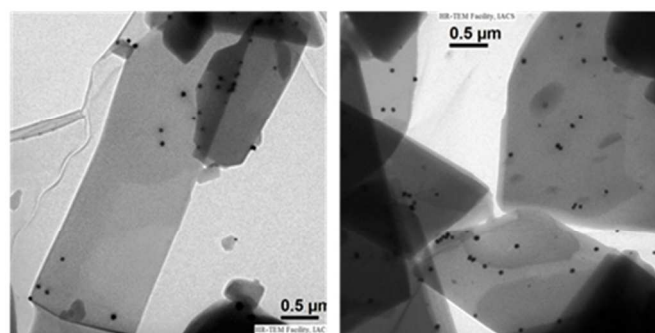

Fig. 4 TEM photographs of AuNPs deposited on the ultra-thin plates of the gel derived from gelator **5**.
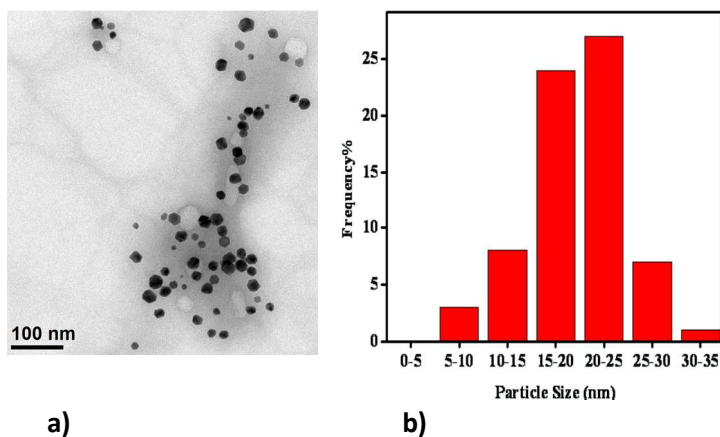
Fig. 5 a) TEM photographs of AuNPs generated on gel **6** and b) the histogram showing the size distribution of the AuNPs.
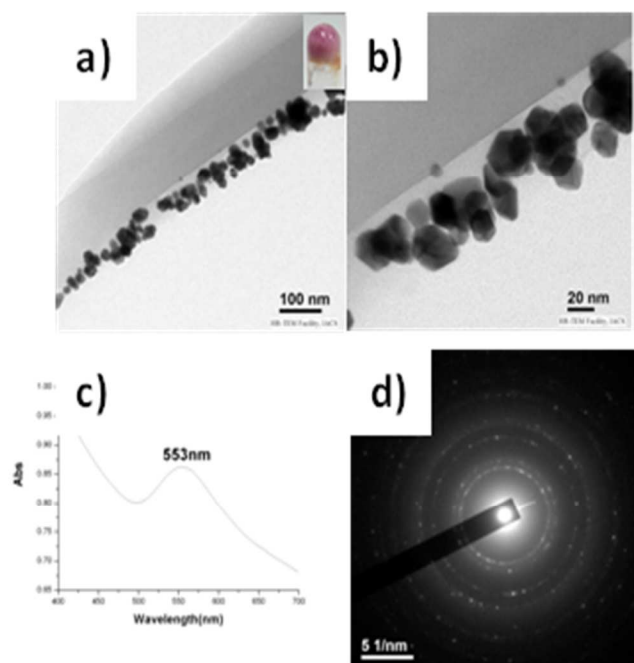

Fig. 6 a) HRTEM photographs of AuNPs embeded on gel network of **2** (inset – typical pink coloured AuNPs within the gel of 2); b) zoomed view of the AuNPs; c) UV-VIS spectrum of the AuNPs displaying surface plasmon band; d) SAED of AuNPs.

XPS spectrum of the AuNPs embedded gel of **6** in DMF/water; shows two peaks at 84.48eV and at 87.74eV (Fig. 7), which correspond to binding energies of Au $4f_{7/2}$ and Au $4f_{5/2}$ electronic states, respectively. It may be noted that the band at 84.48eV due to Au $4f_{7/2}$ is indicative of the presence of both Au(0) and Au(I)

species.[42-45,79-80, 91] The excess Cl$^-$ ions from HAuCl$_4$, xH$_2$0 can well stabilize the generated Au(I) ions.
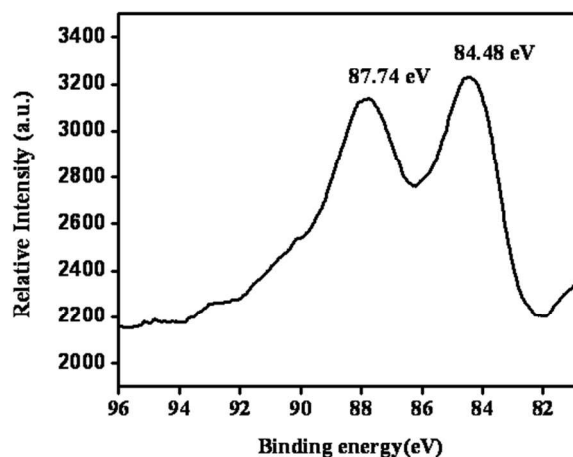

Fig. 7 XPS spectrum of AuNPs embedded on gel of **6** (DMF/water).

Catalytic reduction of p-Nitrophenolate to p-Aminophenolate on the supramolecular gel embedded AuNPs:

AuNPs are well known in catalyzing various reactions.[15,16,71-74] Here, we attempted to use the gel embedded AuNPs in catalyzing the well studied reduction of p-Nitrophenol to p-Aminophenol.[75-78] For this purpose, we chose to work with a DMF/water gel of **6**. When an alkaline (NaOH) solution (2 ml) of p-Nitrophenol (4.3 x 10^{-3} mmol) was placed over a DMF/water gel of **6** containing AuNPs, formation of p-Aminophenol took place; which could be monitored by time-resolved UV-Vis spectroscopy (Fig. 8). Remarkably no external reducing agent such as NaBH$_4$ was required to carry out this conversion of Nitrophenolate to Aminophenolate, which is a novel phenomenon to the best of our knowledge. Similar conversion was obtained on gels containing AuNPs derived from other gelators as well.The yellow color of p-Nitrophenolate changed to colorless (Instets Fig. 6). Blank experimet with p-Nitrophenol in alkaline medium kept on gel bed of **6** made from DMF/water, containing no AuNPs, , resulted in no change of p-Nitrophenolate band at 400nm and there was no change in the yellow color of alkaline p-Nitrophenol as well, indicating no conversion of p-Nitrophenol to p-Aminophenol.
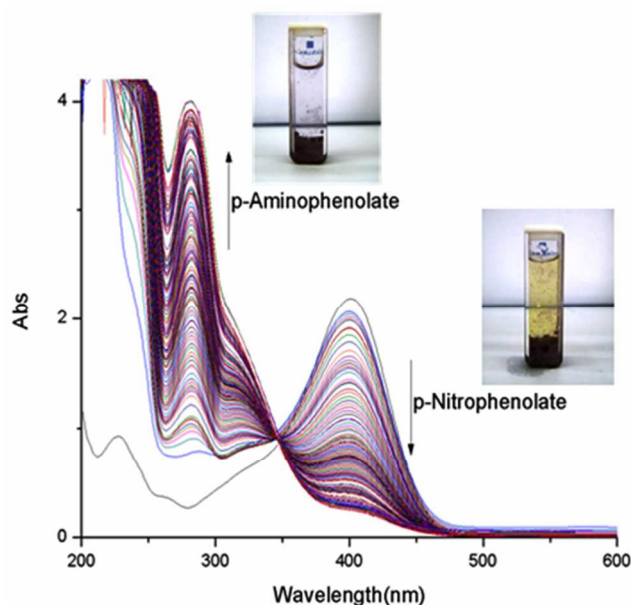
Fig. 8 Time resolved UV-Vis spectra displaying the conversion of p-Nitrophenolate to p-Aminophenolate carried out on gel-embedded AuNPs (DMF/water), produced in **6**. No NaBH$_4$ was added to the reaction. The arrows represent the changes in absorbance of p-Nitrophenolate (decrease in abs.) and p-Aminophenolate (increase in abs.). The time interval for the changes in absorbance was 1 minute. The reaction was carried out at room temperature.

Formation of fluorescent Au nanocluster on changing the gelling solvent:

Changing the gelation-solvent from DMF/water to nitrobenzene produced some remarkable results. We changed the solvent; keeping in mind the fact that, in addition to the reducing and stabilizing role played by the gelator molecules, the solvents viz. DMF or Ethylene Glycol (EG) are reducing in nature and they might play a role in reducing Au^{3+} to Au^0 leading to the formation of AuNPs/AuNCs. [Although no surface plasmon band was found on dissolving HAuCl$_4$.xH$_2$O in these solvents (control/blank experiments with DMF/water and EG/water) ruling out the formation of AuNPs; see Figs. S6, S7)] However, nitrobenzene, is not reducing at all, as compared to above-mentioned solvents, and subsequently, unlikely to play any role in reducing Au^{3+} leading to AuNPs/AuNCs formation. Hence, in nitrobenzene, only the gelator molecules are supposed to be responsible for the AuNP/AuNC synthesis. During the gelation experiments in nitrobenzene, the MGC for the gelators **1-3**, **6**, **7**,

remained the same (5% w/v). Remarkably, for **4** and **5** it came down to 5% (w/v) from 10% (w/v), compared to the case of DMF/water etc. Here, we found that when an aqueous solution of HAuCl$_4$.xH$_2$O, (2ml solution, bearing 1mg/ml of the gold salt) is placed on the gel, within 24 hrs. monodisperse Au clusters of size 2nm or less were formed; as evidenced from HRTEM image (Fig. 9). The AuNCs gave strong emission when excited at 470nm, giving intense fluorescence band at around 521-526nm. (Figs. S12 and S14).The fluorescence intensity was quite stable even in the presence of large excesses of NaCl, KCl and glutathione (See Fig.S15).
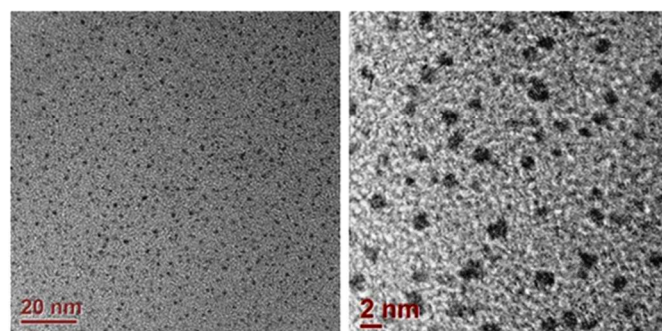

Fig. 9 TEM micrographs of Au nanoclusters (AuNCs) produced from nitrobenzene gel of **6**.

Sensing of Hg by fluorescent Au nanocluster:

Since Hg is one of the most toxic elements, and exposure to all Hg-based materials causes damage to the central nervous system as well as other organ systems, it is important to develop sensitive Hg sensor that can determine Hg in environment, water and food. A number of probes and sensors have been reported for detection of Hg(II).[81-86] Among them are notably promising fluorescent Au nanoclusters (AuNCs) which act as sensors for Hg(II) through quenching of their fluorescence intensity.[87-91] Recently some theoretical studies indicate that, dispersion forces, which are quite strong and specific for closed-shell heavy metal ions like Hg^{+2}(4f^{14}5d^{10}) and Au^{+}(4f^{14}5d^{10}), are further enhanced by relativistic effects.[92-96] Therefore this particular Hg^{+2}-Au^{+} "metallophilic" interaction may be utilized for Hg^{+2} detection/ sensing; which we wanted to take advantage of. This interaction may lead to the formation of HgAu alloy, quenching the fluorescence of Au nanocluster. We observed that the fluorescence of Au nanoclusters get quenched to a significant extent, upon addition of Hg^{+2} ion from an aqueous HgCl$_2$ soln (Figs.10, 11, 12 and S16, S17, S18). The limit of detection (LOD) for Hg^{+2} was found to be 60nM (See

Figs. 10 , 11 and 12). The fluorescence quenching response was found to be more pronounced in dilute solutions of Au NCs than in a concentrated soln. (Fig. S18).
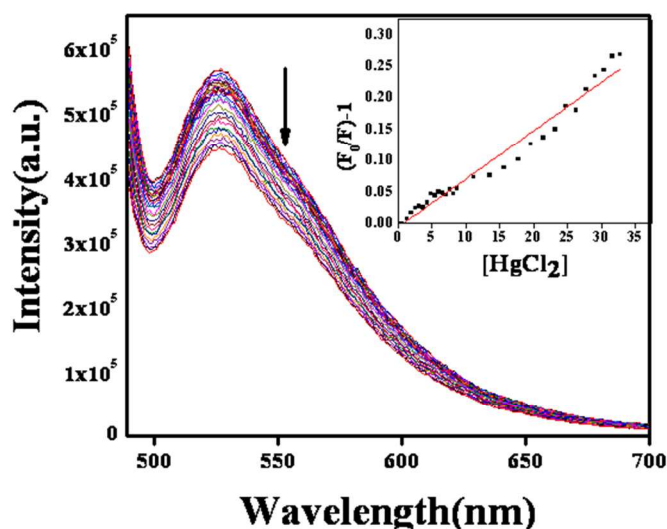

Fig. 10 Quenching of fluorescence in the AuNCs (derived from gel **6**) upon addition of aqueous solution of $HgCl_2$ (starting from 0.6µM to 30µM). Inset: Stern-Volmer plot.
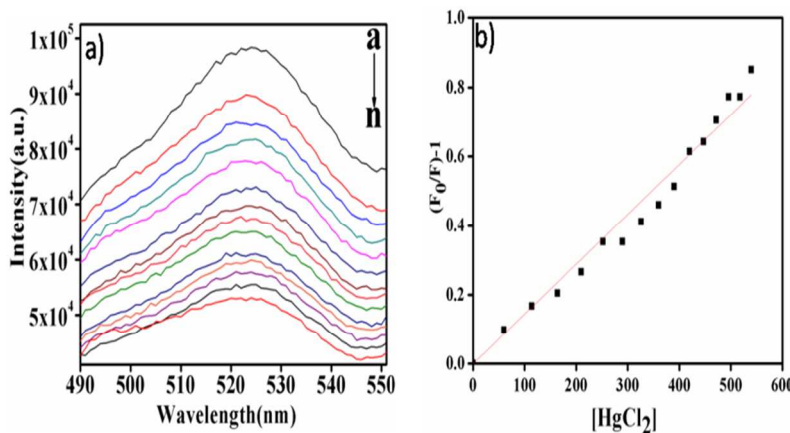

Fig.11 (a)Fluorescence response of AuNCs in presence of different conc. of $HgCl_2$; (a) 0 nM, (b) 60 nM, (c) 114 nM, (d)164 nM, (e) 210 nM, (f) 252 nM, (g) 290 nM, (h) 326 nM, (i) 360 nM, (j) 390 nM, (k) 420 nM, (l) 447 nM, (m) 472 nM, (n) 496 nM; (b) Stern-Volmer plot.
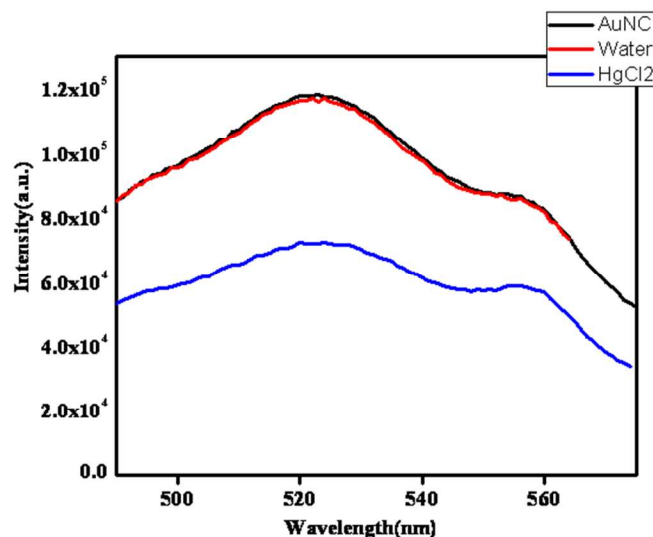

Fig. 12 Quenching of fluorescence of AuNCs upon addition of aq. soln. of $HgCl_2$ (60 nM).This figure forms the basis for determination of limit of detection (LOD) for Hg(II) by AuNCs.

The Limit of Detection (LOD) for Hg(II) was determined in the following manner . Two solutions (2 ml each) of Au nanocluster in aqueous solutions were taken from the same sample of Au in two different PL cuvettes. In the first one, 100 microlitre of water (Millipore Water of resistivity 18.2MΩ.cm) was added and PL measured. In the 2nd, 100 microlitre of aqueous solution of $HgCl_2$ was added to the solution containing Au nanocluster such that the final concentration of $HgCl_2$ became 60 nM in the solution and then its PL measured (Fig. 12). Addition of $HgCl_2$ solution of lower concentration did not produce significant changes in the PL spectrum of the Au nanocluster in comparision to water, as described above.

Fluorescence lifetime decay measurements:

Fluorescence lifetime decay measurements (Fig.13), for AuNCs were done in the absence and presence of the quencher ($HgCl_2$), at different concentrations. The decay curves required a sum of two exponentials for a satisfactory fit. The lifetimes (relative amplitudes) for AuNCs were observed as 0.81 ns (38.5%) and 2.939ns (61.46%); the av. lifetime being 2.12 ns. When the quencher ($HgCl_2$) was added to the above soln; the av. lifetime were found to be 2.16 ns, 2.10 ns, 2.20 ns and 2.29 ns for concentrations (a) 60 nM, (b)1.1 µM, (c) 40 µM and (d) 80 µM of $HgCl_2$ respectively; which were practically no different from the av. lifetime of the AuNCs itself. This indicated that the quenching, here, was a ground state phenomenon or static quenching.[93]
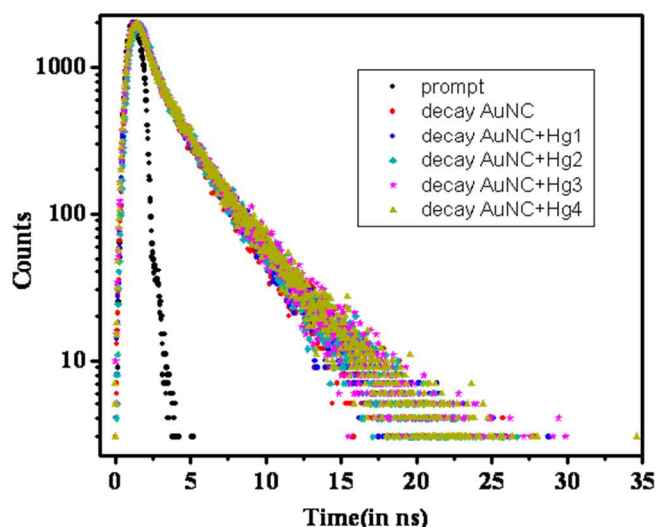
Fig. 13 Fluorescence lifetime measurements (decays) for the AuNCs in aqueous solution were measured with excitation at 450nm; in absence and in the presence of the quencher (HgCl$_2$) at various concentrations. (a) 60 nM, (b)1.1µM, (c) 40 µM and (d) 80 µM.

Conclusions

Thus, a new series of supramolecular gelators derived from bis-pyridyl compounds equipped with hydrogen bonding backbone (urea/amide) have been successfully synthesized and characterized. Remarkably all the gelators are capable of producing AuNPs when solid gold salt or its solution in water is placed over a freshly prepared gel (DMF/water or EG/water or DMSO/water – 1:5 v/v in all the cases) within 12-48 hrs. at room temperature without any exogenous reducing agent. Remarkably, the AuNPs thus synthesized within the gel, derived from all the gelators, are able to catalyze the reduction of p-Nitrophenol to p-Aminophenol at room temperature without use of any external reducing agent like NaBH$_4$ – an observation hitherto unknown to the best of our knowledge. The change of gelation solvent to nitrobenzene gave rise to gels with lower MGC in certain cases and produced stable and fluorescent Au nanoclusters (AuNCs) from aq. soln of HAuCl$_4$, xH$_2$O. The emitting AuNCs display efficient Hg sensing property through their fluorescence quenching, which has been found to be a ground-state phenomenon.

Notes and references

1 Molecular Gels. *Materials with Self-Assembled Fibrillar Networks,* ed. R. G. Weiss and P. Terech, Springer, Dordrecht, The Netherlands; 2005.

2 P. Dastidar, *Chem. Soc. Rev.*, 2008, **37**, 2699-2715;

3 S.Srinivasan, P. A. Babu, S. Mahesh and A. Ajayaghosh, *J. Am. Chem. Soc,* 2009 **,131,**15122–15123.

4, K. K. Kartha, S. S. Babu, S. Srinivasan, and A. Ajayaghosh, *J. Am. Chem. Soc,* **2012**, *134*, 4834-4841.

5 D. Dıaz Dıaz, D. Kühbeck and R. J. Koopmans, *Chem.Soc.Rev.*, 2011, **40**, 427-448.

6 D. Kühbeck, G. Saidulu, K. R. Reddy and D. Diaz Diaz, *Green Chem.,* 2012, **14**, 378-392.

7 B. Escuder, F. R-Llansola and J. F. Miravet, *New J. Chem.,* 2010, **34,** 1044–1054.

8 F. R-Llansola, J.F. Miravet and B. Escuder, *Chem. Commun.,* 2009, 7303-7305.

9 C. Berdugo, J. F. Miravet and B. Escuder , *Chem. Commun.*, 2013, **49**,10608-10610.

10 M. George and R. G. Weiss, *Acc. Chem. Res.,* 2006, **39**, 489–497.

11 K. Sugiyasu, S. Tamaru, M. Takeuchi, D. Berthier, I. Huc, R. Oda and S. Shinkai*, Chem. Commun.*, 2002, 1212-1213.

12 E. D. Sone, E. R. Zubarev and S. I. Stupp, *Angew. Chem. Int. Ed*. 2002, **41**, 1705-1709.

13 Y. Yang, M. Suzuki, S. Owa, H. Shirai and K. Hanabusa, *J. Mater. Chem.*, **2006**, *16*, 1644-1650.

14 P. Xue, R. Lu, Y. Huang, M. Jin, C. Tan, C. Bao, Z. Wang and Y. Zhao, *Langmuir* **2004**, *20*, 6470-6475.

15 M-C. Daniel and D. Astruc, *Chem. Rev.*, 2004, **104**, 293-346.

16 G. J. Hutchings, *Chem. Commun.*,2008, 1148-1164.

17 C. N. R. Rao, G. U. Kulkarni, P. J. Thomas and P. P. Edwards, *Chem. Soc. Rev.*, 2000, **29**, 27-35.

18 D. Das, T. Kar and P. K. Das, *Soft Matter,* 2012**, 8,** 2348-2365.

19 M. Kimura, S. Kobayashi, T. Kuroda, K. Hanabusa and H. Shirai, *Adv. Mater.*, 2004, **16,** 335-338.

20 S. Ray, A. K. Das and A. Banerjee, *Chem. Commun*., 2006, 2816-2818.

21 S. Roy and A. Banerjee, *Soft Matter,* 2011, **7**, 5300-5308.

22 B. Adhikari and A. Banerjee, *Chem.Eur.J.*,2010,**16**,13698-14705.

23 S. Bhattacharya, A. Srivastava and A. Pal, *Angew. Chem. Int. Ed.*, 2006, **45**, 2934-2937

24 H. Basit, A. Pal, S. Sen and S. Bhattacharya, *Chem.-Eur.J.*,2008,**14**,6534-6545.

25 M-O.M. Piepenbrock, N. Clarke and J. W. Steed , *Soft Matter* ,2011,**7**, 2412-2418.

26 C. S. Love, V. Chechik, D. K. Smith, K. Wilson, I. Ashworth and C. Brennan, *Chem. Commun.*, 2005, 1971-1973.

27 M.A. Firestone, M. L. Dietz, S. Seifert, S. Trasobares, D. J. Miller and N. J. Zaluzec, *Small*, 2005, **1**, 754-760.

28 R. N. Mitra and P. K. Das, *J. Phys. Chem. C,* 2008, **112**, 8159-8166.

29 S. Dutta, A. Shome, S. Debnath and P. K. Das, *Soft Matter,* 2009, **5**, 1607-1620.

30 T. Kar, S. Dutta and P. K. Das, *Soft Matter*, 2010, **6**, 4777-4787.

31 D. Das, S. Maity, S. Brahmachari and P. K. Das, *Soft Matter,* 2011,**7**, 7291-7303.

32 J. Y. Yook, G-H Choi and D. H. Suh, *Chem. Commun.*, 2012, **48**, 5001-5003.

33 J-S. Shen, Y-L. Chen, J-L. Huang, J-D. Chen, C. Zhao, Y-Q Zhang, T. Yu, Y. Yang and H-W. Zhang, *Soft Matter,* 2013, **9**, 2017-2023.

34 I. Maity, D. B. Rasale and A. K. Das, *Soft Matter,* 2012, **8**, 5301-5308.

35 P. K. Vemula and G. John*, Chem. Commun.*, 2006, 2218-2220.

36 P. K. Vemula, U. Aslam, V. Ajay Mallia and G. John*, Chem. Mater.*, 2007, **19,**138-140.

37 F. Delbecq, K. Tsujimoto, Y. Ogue and T. Kawai, *Tetrahedron Lett.*, 2013, **54,** 651-656.

38 X. Wang, C.E. Egan, M. Zhou, K. Prince, D. R. G. Mitchell, R. A. Caruso, *Chem. Commun.*,2007, 3060-3062.

39 B. H. Kim, M. J. Hacket, J. Park and T. Hyeon, *Chem. Mater.*, 2014,**26**,59-71.

40 H. Duan and S. Nie, *J.Am.Chem.Soc.*,2007,**129**, 2412-2413.

41 J.Zheng,J.T.Petty and R.M.Dickson,*J.Am.Chem.Soc.*,2003,**125**,7780-7781.

42 L. Shang, N. Azadfar, F. Stockmar, W. Send, V. Trouillet, M. Bruns, D. Gerthsen and G. U. Nienhaus, *Small,* 2011, **7**, 2614-2620.

43 J. Xie, Y. Zheng and J. Y. Ying, *J.Am.Chem.Soc.*, 2009, **131,**888-889.

44 C. Zhou, C. Sun, M. Yu, Y. Qin, J. Wang, M. Kim and J. Zheng, *J.Phys.Chem.C,* 2010, **114,** 7727-7732.

45 Y. Yu, Z. Luo, D. M. Chevrier, D. T. Leong, P. Zhang, D. Jiang and J. Xie, *J.Am.Chem.Soc.*, 2014, **136**, 1246-1249.

46 C-C. Huang, H-Y. Liao, Y-C. Shiang, Z-H. Lin, Z. Yang and H-T.Chang, *J. Mater. Chem.*, 2009, **19**,755-759.

47 M. L. Tran, A. V. Zvyagin and T. Plakhotnik, *Chem.Commun.*,2006, 2400-2401.

48 Y. Shichibu, Y. Negishi, T. Tsukuda and T. Teranishi, *J.Am.Chem.Soc.*, 2005, **127**, 13464-13465.

49 T. H. Lee, J. I. Gonzalez, J. Zheng and R. M. Dickson, *Acc.Chem.Res.*, 2005, **38**, 534-541.

50 J. Zheng, P. R. Nocovich and R. M. Dickson, *Annu. Rev. Phys. Chem.*,2007,**58**, 409-431.

51 J. Zheng, C. Zhang and R. M. Dickson, *Phys.Rev.Lett.*, 2004,**93**,7, 077402(1)-(4).

52 S. Palmal, S. K. Basiruddin, A. R. Maity, S. C. Ray and N. R. Jana, *Chem. Eur. J.*, 2013, **19**, 943-949.

53 P. Byrne, D. R. Turner, G. O. Lloyd, N. Clarke and J. W. Steed, *Cryst.Growth Des.,* 2008, **8**, 3335-3344.

54 Y. Wang, J. Chen and J. Irudayaraj, *ACS Nano,* 2011, **5**, 9718-9725.

55 H-H. Wang, C-A. J. Lin, C-H. Lee, Y-C. Lin, Y-M. Tseng, C-L. Hsieh, C-H. Chen, C-H. Tsai, C-T. Hsieh, J-L Shen, W-H. Chan, W. H. Chang and H-I.Yeh, *ACS Nano,* 2011, **5**, 4337-4344.

56 M. Yu, C. Zhou, J. Liu, J. D. Hankins and J. Zheng, *J. Am. Chem. Soc.*,2011, **133**, 11014–11017.

57 L. Shang, S. Dong and G. U. Nienhaus, *Nano Today,*2011,**6**, 401-418.

58 X. Tu, W. Chen, X. Guo, *Nanotechnology,* 2011,**22** ,095701.

59 Y-C. Shiang, C-C. Huang , H-T. Chang, *Chem.Commun.*, 2009, 3437-3439.

60 T. K. Adalder,D. P. Kumar and P. Dastidar, *Cryst. Growth De.s,* 2014, **14**, 11–14.

61 N. N. Adarsh, D. K. Kumar and P. Dastidar, *Cryst.Eng.Commun.*, 2008, **10**, 1565-1573.

62 N.N.Adarsh and P.Dastidar, *Cryst. Growth Des.*, 2010, **10**, 483-487.

63 Z.Qin, M.C.Jenings and R.J.Puddephatt, *Inorg. Chem.*, 2003, **42**, 1956-1965.

64 Designing Functional Coordination Polymers and Complexes for Selective Anion Separation and Guest Inclusion: A Crystal Engineering Approach. Thesis submitted for Degree of Doctor of Philosophy in Science, of Jadavpur University by N.N.Adarsh in December 2010.

65 S. R. Raghavan and B.H. Cipriano in *Molecular Gels. Materials with Self-Assembled Fibrillar Networks*, ed. R. G. Weiss and P. Terech, Springer, Dordrecht, The Netherlands, 2005, Ch. 8, 241-252.

66 Y. Zhou, D. Wang and Y. Li, *Chem. Commun.*, 2014, **50**, 6141-6144.

67 L-F. Zhang, S-L. Zhong and A-W. Xu, *Angew.Chem..Int. Ed.* 2013, **52**, 645-649

68 T. K. Sau and C. J. Murphy, *J.Am.Chem.Soc.*, 2004, **126**, 8648-8649.

69 S. Chen, Z. L. Wang, J. Ballato, S. H. Foulger and D. L. Carroll, *J.Am.Chem.Soc.*, 2003, **125**, 16186-16187.

70 E. Hao, R. C. Bailey, G. C. Schatz, J. T. Hupp and S. Li , *Nano Lett.,* 2004, **4**, 327-330.

71 C. D. Pina, E. Falleta, L. Prati and M. Rossi, *Chem. Soc. Rev.*,2008, **37**, 2077-2095.

72 M. Haruta, *Nature,* 2005, **437**,1098-1099.

73 M. Brust,and G. J. Gordillo, *J.Am.Chem.Soc.*, 2012,**134**,3318-3321.

74 A. Corma and P. Serna, Science, 2006, **313**,332-334.

75 Z. W. Seh, S. Liu, S-Y Zhang, K. W. Shah and M-Y Han, *Chem. Commun.*, 2011, **47**, 6689-6691.

76 H. Yamamoto, H. Yano, H. Kouchi, Y. Obora, R. Arakawa and H. Kawasaki, *Nanoscale,*2012, **4**, 4148-4154.

77 S. Panigrahi, S. Basu, S. Praharaj, S. Pande, S. Jana, A. Pal, S. K. Ghosh and T. Pal, *J.Phys.Chem.C,* 2007, **111**, 4596-4605.

78 K. Layek, M. Laksmi Kantam, M. Shirai, D.N-Hamane, T. Sasaki, H. Maheswaran, *Green Chem.*, 2012, **14**, 3164-3174.

79 C. Zhou, C. Sun, M. Yu, Y. Qin, J. Wang, M. Kim and J. Zheng, *J.Phys.Chem.C,* 2010,**114**,7727-7732.

80 Y. Negishi, K. Nobusada, and T. Tsukuda, *J.Am.Chem.Soc.*, 2005, **127**, 5261-5270.

81 E. M. Nolan , S. J. Lippard, *Chem. Rev.,* 2008, **108**, 3443-3480.

82 G. K. Darbha, A. K. Singh, U. S. Rai, E. Yu, H. Yu and P. C. Ray, *J.Am.Chem.Soc.*,2008, **130**, 8038-8043.

83 C-C. Huang and H-T Chang, *Anal. Chem.*, 2006, **78**, 8332-8338.

84 X. Xue, F. Wang and X. Liu, *J.Am.Chem.Soc.*, 2008, **130**, 3244-3245.

85 J-S Lee, M. S. Han and C. A. Mirkin, *Angew.Chem.Int.Ed.,* 2007, **46,** 4093-4096.

86 P. Mahato, A. Ghosh, S. Saha, S. Mishra, S. K. Mishra and A. Das, *Inorg.Chem.*,2010, **49**, 11485-11492.

87 J. Xie, Y. Zheng, J. Y. Ying, *Chem.Communn.*, 2010, **46**, 961-963.

88 C-C. Huang, Z. Yang, K-H. Lee and H-T. Chang, *Angew.Chem.Int.Ed.,* 2007, **46,** 6824-6828.

89 Y-H. Lin and W-L Tseng, *Anal. Chem.*, 2010, **82**, 9194-9200.

90 D.Hu, Z. Sheng, P. Gong, P. Zhang and L. Cai, *Analyst,* 2010, **135**, 1411-1416.

91 H. Wei, Z. Wang, L. Yang, S. Tian, C. Hou ,Y. Lu, *Analyst* ,2010, **135,** 1406-1410.

92 A. Burini, J. P. Fackler, Jr., R. Galassi, T. A. Grant, M. A. Omary, M. A. Rawashdeh-Omary, B. R. Pietroni and R. J. Staples, *J.Am.Chem.Soc.*,2000, **122**, 11264-11265.

93 L. H. Pignolet, D.A.Krogstad in Gold: Progress in Chemistry, Biochemistry and Technology (Ed.: H. Schmidbaur), Wiley, New York, 1999, 429-493.

94 R. Wesendrup and P. Schwerdtfeger*, Angew.Chem.Int.Ed.,*2000, **39,** 907-910.

95 R. Wesendrup, J.K. Laerdahl, and P. Schwerdtfeger, *J.Chem.Phys.*, 1999, **110**, 9457-9462.

96 P. Pyykkö, *Angew. Chem. Int. Ed.,* **2004**, *43*, 4412 –4456.

97 J. R. Lakowicz, Principles of Fluorescence Spectroscopy; Springer: New York, 2006.