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Au microparticles mediated construction of a logic based dual channel molecular keypad lock†

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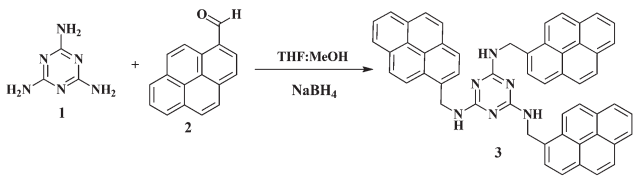
New melamine based ligand 3 with pyrene as a fluorophore is synthesized and characterized. The sequential addition of Au^{3+} ions and ascorbic acid to the solution of 3 in EtOH–H_2O (9.5 : 0.5 v/v) generates gold microparticles (AuMPs). However, the particle size distribution and fluorescence behaviour on sequential additions are different and contribute to the construction of a new logic based molecular dual channel keypad lock system.

Optical technologies based on Au micro/nanoparticles have attracted considerable attention because of their unique properties of stability, biocompatibility and high extinction coefficients.[1] Due to these unique optical properties, Au particles are widely used in areas like materials science.[2] Recently, there has been a lot of interest in the development of molecular logic systems based on Au particles. Jiang *et al.* reported resettable and multi-readout logic systems capable of logic operations based on aggregation of spiropyran with Au particles in aqueous media.[3] Chen *et al.* reported a colorimetric logic gate based on Au particles. In the above reports the optical properties utilized were predominantly based on UV-vis spectroscopy.[4] However, the use of fluorescence for signalling the optical events is more significant due to its very high sensitivity. In addition to this, the present scenario demands the generation of feasibility to integrate molecular logic gates into some decision making devices.

Thus, keeping in view the significance of fluorescence spectroscopy and its application in construction of logic based molecular devices with Au micro/nanoparticles, we designed and synthesized ligand **3** (*vide infra*) based on melamine containing pyrene as fluorogenic units (Scheme 1). The sequential addition of Au^{3+} ions and ascorbic acid to the solution of **3** in EtOH–H_2O (9.5 : 0.5 v/v) generates gold microparticles (AuMPs). However, the fluorescence behaviour and particle size distribution on sequential additions are different and contribute to the construction of a new type of logic based dual channel molecular keypad lock system. A keypad lock is an electronic device which is capable of processing password entries, hence access to an object or data can be restricted to a limited number of people.[5] Molecular devices which can distinguish between the sequences of different chemical inputs are expected to be better than simple logic gates. The development of such a molecular scale keypad lock is particularly an attractive goal as it represents a new approach for protecting information at the molecular scale. These photonic devices can be useful in futuristic applications such as micro-computing. To the best of our knowledge a dual channel molecular keypad lock using two different inputs and two outputs mediated by formation of Au microparticles is unprecedented in the literature.



Scheme 1 Synthesis of ligand **3**.

Condensation of melamine **1** with pyrene-1-carboxaldehyde **2** (ϕ_s = 0.76)[6] and *in situ* reduction of the resultant Schiff base with sodium borohydride furnished compound **3** in 82% yield. The structure of ligand **3** was confirmed from its spectroscopic and analytical data (see ESI S5–S7†). The ^{1}H NMR spectrum of compound **3** showed one doublet (6H) for –CH_2 protons, one triplet (3H) for –NH protons, and three triplets (12H, 12H, 3H) for aromatic protons of pyrene respectively confirming its structure.

The fluorescence emission spectrum of chemosensor **3** (3 ml of 1 × 10^{-3} mmol) showed an emission band (ϕ_s = 0.79) at 395 nm in EtOH–H_2O (9.5 : 0.5 v/v) buffered with HEPES[7] (pH = 7). On addition of increasing amounts of Au^{3+} ions (1.36 mmol) to the solution of ligand **3** in EtOH–H_2O

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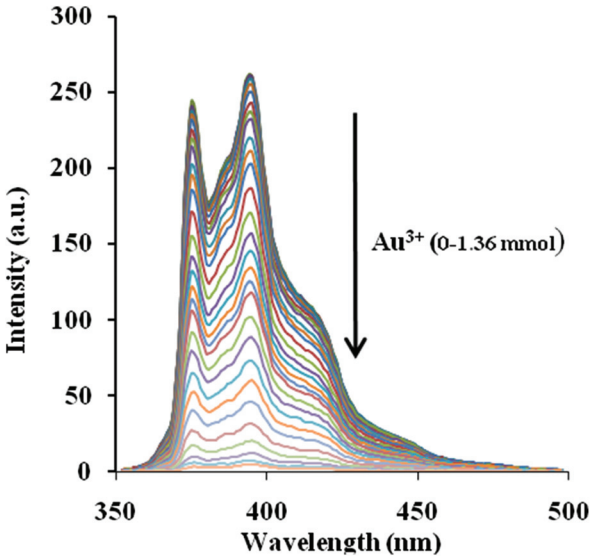

Fig. 1 Fluorescence response of ligand **3** (3 ml of 1 × 10^{-3} mmol), λ_{ex} = 342 nm in EtOH–H_2O (9.5 : 0.5 v/v) on addition of Au^{3+} ions.

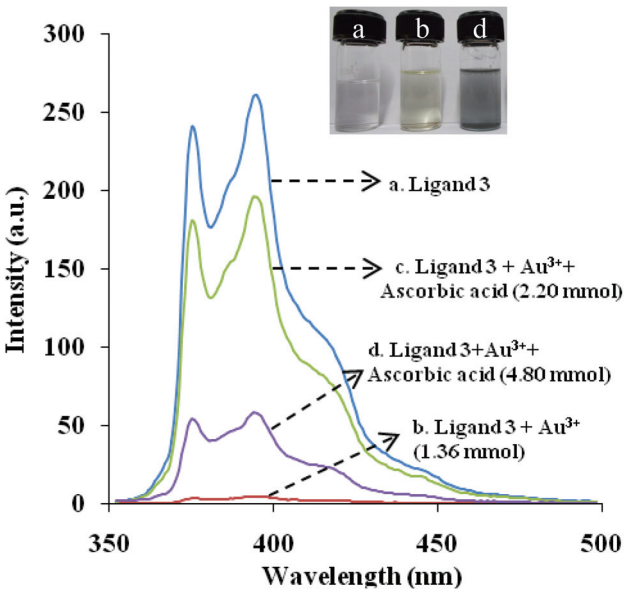

Fig. 2 (a) Fluorescence spectra of ligand **3** (3 ml of 1 × 10^{-3} mmol), λ_{ex} = 342 nm in EtOH–H_2O (9.5 : 0.5 v/v), (b) on addition of Au^{3+} ions (1.36 mmol), (c) on addition of ascorbic acid (2.20 mmol) to the same solution, (d) on further addition of ascorbic acid (2.60 mmol). The inset shows the naked eye changes.

(9.5 : 0.5 v/v), quenching of the emission band was observed (Fig. 1) along with a colour change from colorless to light yellow (inset of Fig. 2). This quenching of the fluorescence emission band is attributed to the binding of Au^{3+} ions to the imino nitrogen atoms of **3** resulting in reverse photo-induced electron transfer (PET) from Au^{3+} ions to **3** thus, suggesting the formation of a complex between Au^{3+} ions and **3**.[8]

The formation of the complex between **3** and Au^{3+} ions is confirmed with the help of ^{1}H NMR, mass and IR spectral analysis. ^{1}H NMR spectral analysis of **3** in the presence and absence of 1.0 equiv. of $AuCl_3$ was carried out in DMSO-d_6 (see ESI S5 and S14†). On addition of Au^{3+} ions to the solution of **3** in DMSO-d_6, –NH protons of **3** disappeared indicating the binding of Au^{3+} ions to amino nitrogen with simultaneous deprotonation of –NH protons (see ESI S5 and S14†). We have also synthesized and characterized a complex between **3** and Au^{3+} ions (for synthetic details see ESI S4†). A parent ion peak shown by this complex in the mass spectrum at *m*/*z* 1015.7028 corresponds to the species (ligand **3** (–3H)·Au^{3+}·3H_2O named hereafter as **3**·Au^{3+} complex), confirming the formation of a complex between ligand **3** and Au^{3+} ions (see ESI S8†). We assume that the **3**·Au^{3+} complex will exhibit square planer geometry which will be supported by the presence of H_2O molecules.[9] The IR spectrum of **3** showed an –NH stretching band at 3300 cm^{-1}, however no such band was observed in the case of the **3**·Au^{3+} complex (see ESI S15†) which also supports NMR data. For conversion of Au^{3+} ions of the **3**·Au^{3+} complex into Au particles, we selected ascorbic acid as a reducing agent due to its biodegradability and low toxicity.[10] We observed that on addition of 2.2 mmol of ascorbic acid to the solution of {**3**+ Au^{3+} ions (1.36 mmol)} in EtOH–H_2O (9.5 : 0.5 v/v), there was a revival in fluorescence intensity (Fig. 2). This could be attributed to the decomplexation of the **3**·Au^{3+} complex on addition of ascorbic acid. The colour of the solution also changed from yellow to colorless. However, the incomplete revival of fluorescence intensity reveals that the decomplexation is not 100%. On further addition of ascorbic acid (4.8 mmol), the revived Au^{3+} ions were reduced to AuMPs which again caused significant fluorescence quenching.[11] This was marked by color change from light yellow to black. However, the final fluorescence emission remains in 'on state'.

The formation of AuMPs is confirmed with the help of TEM analysis (Fig. 3). The TEM image of **3**·Au^{3+} shows a well organized network (Fig. 3a). On addition of ascorbic acid the TEM image showed that the organized network compacts into a mass with simultaneous formation of AuMPs. The particle size distribution in the case of ligand **3** and ligand **3** + Au^{3+} ions was <500 nm as measured with the help of DLS experiments (see ESI S9 and S13†). The large size for the ligand particles observed in the DLS data could be ascribed to the formation of aggregates of **3** due to intermolecular hydrogen bonding.[12] In contrast, in the case of ligand **3** + Au^{3+} + ascorbic acid particle size distribution was >500 nm (see ESI S10†) as observed from DLS data (fluorescence behaviour *vide infra*).

Nowadays, microscale devices are being constructed with a bottom up approach.[13] The development of molecular devices has inspired chemists to use small molecules as versatile building blocks for devices for a wide range of digital functionalities from data storage, numerical processing, quiz games to password entries.[14] However, the Au particles mediated system for memory storage devices is still unexplored. To examine our molecular system **3** for construction of AuMPs mediated sequential logic devices (memory storage), we carried out the experiments by inverting the order of addition of both the inputs *i.e.* adding ascorbic acid first, followed by addition of

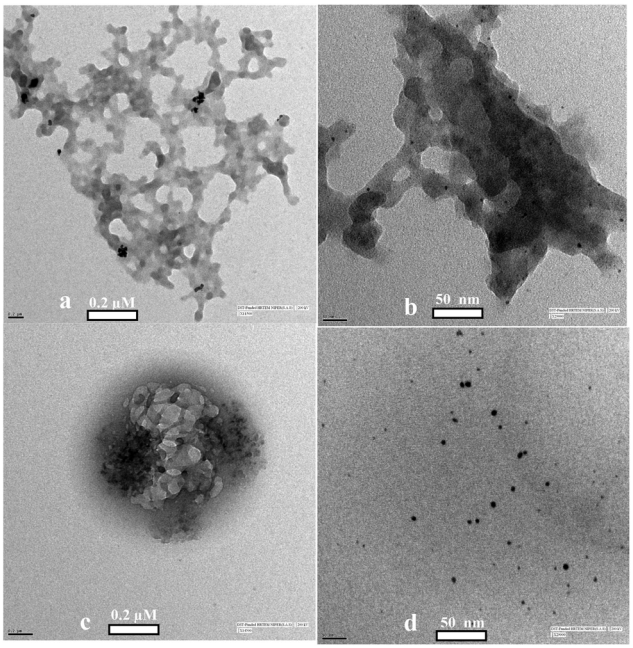

Fig. 3 TEM images of samples. (a) **3** + Au^{3+} ions, (b) **3** + Au^{3+} + ascorbic acid (Au^{3+} ions followed by ascorbic acid), (c) **3** + ascorbic acid, (d) **3** + ascorbic acid + Au^{3+} ions (ascorbic acid followed by Au^{3+} ions).

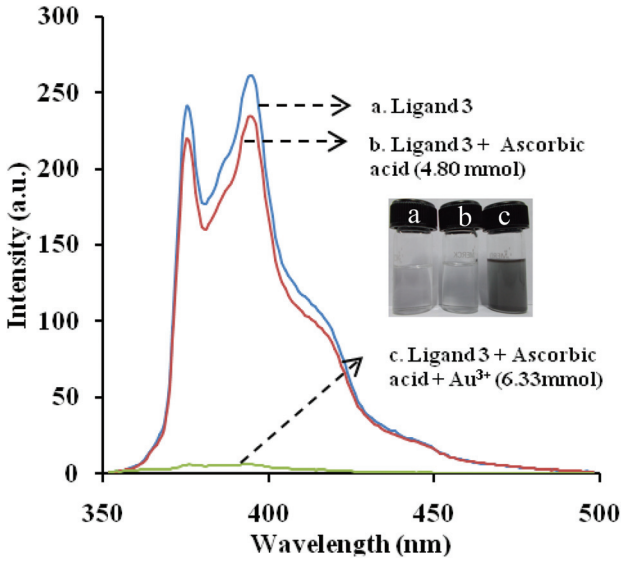

Fig. 4 (a) Fluorescence spectra of ligand **3** (3 ml of 1 × 10^{-3} mmol), l_{ex} = 342 nm in EtOH–H_2O (9.5 : 0.5 v/v), (b) in the presence of ascorbic acid (4.80 mmol), (c) further addition of Au^{3+} ions (6.33 mmol). The inset shows the naked eye changes.

Au^{3+} ions. On addition of ascorbic acid to the solution of ligand **3** [EtOH–H_2O (9.5 : 0.5 v/v)], no change in the fluorescence emission spectrum was observed as practically there was no interaction between ligand **3** and ascorbic acid. This was also proved with TEM analysis (Fig. 3). On addition of Au^{3+} (6.33 mmol *vs.* **3**) to the solution containing **3** and ascorbic acid, complete quenching of the fluorescence emission was observed (Fig. 4). In addition, colour of the solution changed to black. The quenching of the fluorescence is attributed to the formation of a **3**·Au^{3+} complex. The black colour appeared as the ascorbic acid present in the solution also reduces the Au^{3+} ions. The results were also confirmed by TEM analysis (Fig. 3). The particle range for sequence *viz.* ligand **3** + ascorbic acid and ligand **3** + ascorbic acid + Au^{3+} ions is <500 nm as observed with DLS data (see ESI S11 and S12† respectively).

Thus, based on the above experiments we propose that the nature of AuMPs formed in both the sequences is different. In the sequence (**3** + Au^{3+} + ascorbic acid), the ascorbic acid reduces the Au^{3+} ions which are in complexed state with ligand **3**, therefore the binding ligand establishes an equilibrium during the reduction reaction which enables careful control of the size.[15] In addition, the ligand also provides steric stabilization by binding to the surface of growing gold microparticles (Fig. 3b). In contrast, in the sequence (**3** + ascorbic acid + Au^{3+}), the $AuCl_3$ is directly added to the solution containing ascorbic acid and the reduction process is not regulated by ligand **3** (Fig. 3d). The large difference in the lowering of the PDI of the sequence (**3** + Au^{3+} + ascorbic acid) 0.3 in comparison to the PDI of (**3** + ascorbic acid + Au^{3+}) 0.9 also accounts for the controlled formation of AuMPs from their mother solutions (**3** + Au^{3+}) (PDI = 1.0) and (**3**+ ascorbic acid) (PDI = 1.0) respectively accounts for the controlled synthesis of AuMPs in the sequence (**3** + Au^{3+} + ascorbic acid).

Thus, based on the above experiments we envisaged our system for the construction of a new dual channel keypad lock. In this dual channel keypad lock the channel 1 (CH1) reveals the output corresponding to the emission wavelength at 395 nm. The channel 2 (CH2) reveals the output in terms of the particle size distribution range. The presence of such dual channels adds to the complexity of the keypad lock which is a desirable feature from an application point of view. To acquire a keypad lock based on boolean arithmetic, we designated Au^{3+} ions (password entry **A**) and ascorbic acid (password entry **V**) as inputs. The emission wavelength at 395 nm is designated output 1 (channel 1) ['on state' corresponds to password entry **N** and '*off* state' corresponds to the password entry **F**) and the particle size distribution is designated output 2 (channel 2) (particle size distributions >500 nm and <500 nm have been assigned logic values '1' and '0' and correspond to the password entries **$** and **#** respectively). Applying the binary logics using the above inputs the truth Table 1 has been constructed. The fluorescence output and DLS behaviour

Table 1 Truth table with two inputs and two outputs

Sr. No.	Input 1 Au^{3+} ions	Input 2 Ascorbic acid	Output 1 Channel 1 Emission wavelength at 395 nm	Output 2 Channel 2 Particle size distribution
1	0	0	1	0
2	1	0	0	0
3	0	1	1	0
4	1a	1b	1	1
5	1b	1a	0	0

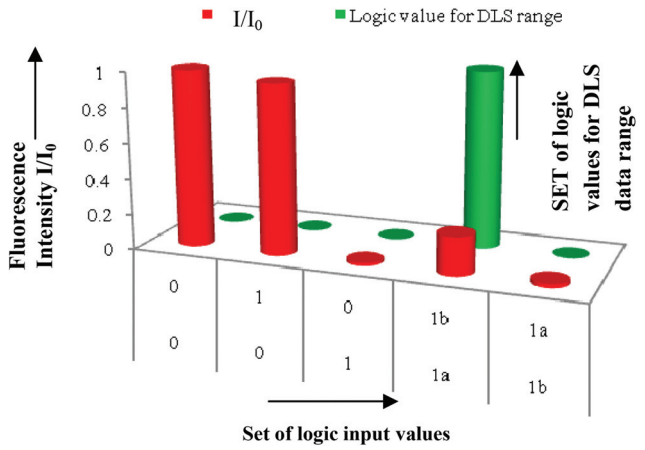

Fig. 5 Fluorescence output I/I_0 (red bar) and output with logic assignment for the DLS range (green bar) resulting from addition of two chemical inputs in a sequential manner corresponding to truth Table 1. 'I' denotes the fluorescence intensity after addition of the input and I_0 is the initial fluorescence intensity *i.e.* before the addition of any chemical input. It denotes that there is only one input combination *i.e.,* combination 4 of truth Table 1 when both the outputs are simultaneously present.

on addition of different input combinations has been shown in Fig. 5.

Based on these input and output combinations, a dual channel molecular keypad lock (Fig. 6) is proposed. The lock is programmed in such a way that it opens when both the outputs are in logic state (1,1) (see the combination value four from truth Table 1 and Fig. 5). For the first input sequence Au^{3+} ions (input 1) followed by ascorbic acid (input 2), the fluorescence is in 'on' state (output 1) with particle size >500 nm (output 2). This generates the password entry '**AVN$**'. On inverting the input sequences, ascorbic acid (input 1) followed by Au^{3+} ions (input 2), the fluorescence is in 'off' state (output 1) with particle size <500 nm (output 2). This generates the password entry '**VAF#**'. On addition of single inputs Au^{3+} ions (input 1) the fluorescence is in 'off' state (output 1) with particle size <500 nm (output 2) and '**AF#**' is the password key

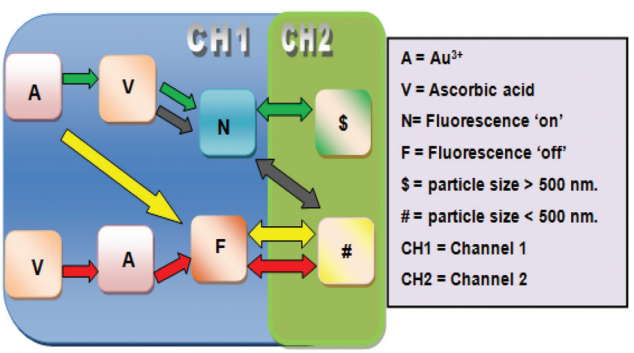

Fig. 6 Keypad lock to access secret code '**AVN$**'. Yellow arrows represent the logic set 2 (truth Table 1). Grey arrows represent logic set 3 (truth Table 1). Green arrows represent the logic set 4 (truth Table 1). Red arrows represent the logic set 5 (truth Table 1).

generated. Inversely, addition of only ascorbic acid (input 2) keeps the fluorescence in 'on' (output 1) state with particle size <500 nm (output 2). This generates the password key '**VN#**'. The four password keys '**AVN$**', '**VAF#**', '**AF#**' and '**VN#**' generate output logic values (1,1), (0,0), (0,0) and (1,0) respectively (truth Table 1). As only the output value (1,1) is the combination to open the lock the password entry '**AVN$**' is the only key to open the lock.

Conclusions

To conclude, we have developed a new fluorescent molecular system which acts as a platform to generate AuMPs and behaves as a dual channel molecular keypad lock. All the molecular events were carried out in mixed aqueous media which makes this system biocompatible. The generation of AuMPs in a sequential manner provides a platform to store information at a micro-scale. Harnessing the principles of electronics to such logic based sequential devices can generate various applications in materials sciences.

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