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# Dipyrromethane as a new organic reagent for the synthesis of gold nanoparticles: preparation and application

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Abstract Condensation reaction of several ketones with pyrrole in the presence of ferric hydrogen sulfate as a green homogenous acidic catalyst furnished the corresponding pure dipyrromethanes in good yields. Gold nanoparticles were produced through reduction of HAuCl<sub>4</sub> with substituted dipyrromethanes as new reducing agents at room temperature with the exclusion of any capping agent or surfactant. Gold nanoparticles were characterized by transmission electron microscopy, scanning electron microscopy, XRD and UV-visible absorption spectroscopic measurements. It is proposed that in situ formed oxidative products of dipyrromethane, such as polydipyrromethane could serve effectively as a capping agent to preferably adsorb the {111} facets of gold crystals during the reduction process, which leads to the formation of gold nanoparticles.

**Keywords** Gold · Nanoparticles · Dipyrromethanes · Ferric hydrogen sulfate · Green conditions

# Introduction

During the past decades, metal nanostructures have attracted extensive interests because of the different performances from their bulk counterparts and also their unique optical, electronic, photonics, magnetic, biologic, catalytic properties [1–3]. With regard to noble metal nanoparticles, gold nanoparticles (Au-NPs) have been a major field of study, because of their strong surface plasmon resonance, potential applications in medical diagnostics, imaging, and therapeutic treatments, application as scaffolds for molecular recognition of elements and molecules [4], in optoelectronics and data storage [5], and in nanotechnology with molecular switches [6]. Gold nanoparticles can be synthesized in a range of shapes and sizes such as nanorods [7], nanotriangles [8], nanocubes [9], nanocages [10], nanonetworks [11–13], nanoplates [14], and nanowires [11]. Typically, gold nanoparticles are generally obtained by chemical reduction of tetrachloroauric acid using sodium borohydride [15, 16], sodium citrate, sodium ascorbate [17], sodium oxalate [18], hydrazine [19], hydroquinone [20], cysteine [21] or ionic liquids [22]. It has been noted that the variation of particle growth medium plays a profound role in controlling the size and colloidal stability. However, an alternative way for the formation of gold nanoparticles from AuCl<sub>4</sub><sup>-</sup> is to choose an efficient reducing as well as a capping agent so that the relative rates between nucleation and growth are well controlled.

On the other hand, dipyrromethanes are crucial intermediates for the synthesis of substituted porphyrins, expanded porphyrins, porphyrin analogs (dipyrrins, calixpyrroles, chlorins, corroles) and polypyrrolic polymers that are useful in chemistry, physics, biology, medicine and engineering. Dipyrromethanes are also widely used as ligands in organometallic synthesis and catalysis [23–25]. Therefore, the growing interest on these molecules led synthetic chemists to find new routs in order to improve reaction conditions. Most of the methods have reported the condensation of an aldehyde or ketone and pyrrole using various combinations of acids and solvents, such as *p*-toluenesulfonic acid (in MeOH or toluene) [26, 27], acetic acid (in DMF or THF) [28, 29], trifluoroacetic acid (in TFA) [30], TiCl<sub>4</sub> (in CH<sub>2</sub>Cl<sub>2</sub>) [31], SnCl<sub>4</sub> (in CH<sub>2</sub>Cl<sub>2</sub>) [32],

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BF<sub>3</sub>·etherate (in CH<sub>2</sub>Cl<sub>2</sub>) [33], aqueous HCl (in THF) [34] and resins [35], etc. However, among the above catalysts, some are expensive, some are inconvenient to use and some gave a low yield of reaction. Also these methods usually involve a final workup that requires, at least, the distillation of the excess pyrrole. On the other hand, chemists have great interest in developing an efficient way for the preparation of organic compounds by using environmentally feasible reagents and solvents. Recently, ferric hydrogen sulfate is reported to be an environmentally friendly and heterogeneous acidic catalyst. Ferric hydrogen sulfate is an inexpensive, non-toxic, stable, and efficient catalyst for various transformations [36] and can be easily prepared from commercially available starting materials [37].

In this study, we have used a catalytic amount of ferric hydrogen sulfate to condense pyrrole with ketones in the absence of any organic solvent, which provides an efficient method to prepare different substituted dipyrromethanes in aqueous and green conditions and then we have developed a facile route for the synthesis of gold nanoparticles by simply adding a typical dipyrromethane as a new and effective reducing agent to an aqueous solution of HAuCl<sub>4</sub> at room temperature with the exclusion of any other capping agent or surfactant. To the best of our knowledge, the use of dipyrromethane as an organic reducing reagent in the synthesis of gold nanoparticles under mild conditions has not been reported in the literature.

## Experimental

#### Materials and physical methods

Gold chloride trihydrate (HAuCl<sub>4</sub>·3H<sub>2</sub>O) was purchased from Aldrich and used without purification. Other chemical compounds used in this research were purchased from Merck. All aqueous solutions were prepared from Millipore water (resistivity, 18 MX; Millipore Systems). Melting points were recorded on an Electrothermal type 9100 melting point apparatus. The 1H NMR (100 MHz) spectra were recorded on a Bruker AC100 spectrometer. Elemental analysis was obtained on a Thermo Finnigan Flash EA microanalyzer. The FT-IR spectra were obtained on an Avatar 370 FT-IR Thermo Nicolet spectrometer. UV-visible (UV-vis) absorption spectroscopic measurements were recorded on a UV-vis spectrometer, Shimadzu UV1700, using quartz cells of 1 cm path length. Transmission electron microscopic (TEM) images of the nanoparticles were taken with a LEO 912AB instrument operated at an accelerating voltage of 120 kV with line resolution of 0.3 nm at room temperature. The samples for TEM measurements were prepared by placing a droplet of the colloidal solution onto a carbon-coated copper grid and allowing it to dry in air naturally. Based on the TEM images we determined the size distributions of the final product by counting at least 300 particles. Scanning electron microscopy (SEM) images were recorded by using a LEO-1530VP field-emission scanning electron microscope with an accelerating voltage of 5.0 kV and the samples were deposited on silicon substrates, which were also used for elemental analysis conducted by energy-dispersive X-ray spectrograph (EDX) attached to the SEM. Powder X-ray diffraction pattern (XRD, D/Max-RA, Cu K $\lambda$ , 40 kV, 30 mA) was taken from the sample prepared by dropping 200 µl of the products dispersed in water on a silicon substrate and allowing the solvent to evaporate spontaneously at ambient temperature.

#### Synthesis of substituted dipyrromethanes

In a typical experiment, pyrrole (0.25 ml, 2 mmol) was added to a suspension of 3-pentanone (0.18 ml, 1 mmol) in water (5 ml), followed by slow addition of  $Fe(HSO_4)_3$  (36 mg, 0.1 mmol). After refluxing for 50 min, the reaction mixture was extracted with chloroform (2 × 25 ml) and washed with water (2 × 25 ml). The organic phase was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and the solvent was relatively pure, but it can be further purified by recrystallization with ethanol:water (20:1).

*Meso*-dimethyl-2,2'-dipyrromethane **1**: yield 71 %, mp: 56–58 °C [**38**]. <sup>1</sup>HNMR (solvent: CDCl<sub>3</sub>; internal standard: TMS):  $\delta = 1.67$  (6H, s, C**H**<sub>3</sub>-C), 6.08 (2H, m, pyrrole-H), 6.20 (2H, m, pyrrole-H), 6.64 (2H, m, pyrrole-H), 7.88 (2H, bs, N**H**). FT-IR (cm<sup>-1</sup>; group): (3,380, N–H).

*Meso*-diethyl-2,2'-dipyrromethane **2**: yield 68 %, mp: 108–110 °C [**39**]. <sup>1</sup>HNMR (solvent: CDCl<sub>3</sub>; internal standard: TMS):  $\delta = 0.68$  (6H, t, J = 7.2 Hz, CH<sub>3</sub>-CH<sub>2</sub>-C), 1.92 (4H, q, J = 7.2 Hz, CH<sub>3</sub>-CH<sub>2</sub>-C), 6.11 (4H, m, pyrrole-H), 6.61 (2H, m, pyrrole-H), 7.65 (2H, bs, NH). FT-IR (cm<sup>-1</sup>; group): (3,371, N–H).

*Meso*-ethyl-*meso*-methyl-2,2'-dipyrromethane **3**: yield 57 %, mp: 103–105 °C. <sup>1</sup>HNMR (solvent: CDCl<sub>3</sub>; internal standard: TMS):  $\delta = 0.81$  (3H, t, J = 7.1 Hz, CH<sub>3</sub>-CH<sub>2</sub>-C), 1.52 (3H, s, CH<sub>3</sub>-C), 1.98 (2H, q, J = 6.9 Hz, CH<sub>3</sub>-CH<sub>2</sub>-C), 5.98 (2H, m, pyrrole-H), 6.14 (2H, m, pyrrole-H), 6.67 (2H, m, pyrrole-H), 7.75 (2H, bs, NH). FT-IR (cm<sup>-1</sup>; group): (3,388, N–H).

*Meso*-diisopropyl-2,2'-dipyrromethane **4**: yield 55 %, mp: 112–114 °C. <sup>1</sup>HNMR (solvent: CDCl<sub>3</sub>; internal standard: TMS):  $\delta = 1.57$  (12H, d, J = 7.4 Hz, (CH<sub>3</sub>)<sub>2</sub>-CH-C), 1.11–1.30 (2H, m, (CH<sub>3</sub>)<sub>2</sub>-CH-C), 5.92 (2H, m, pyrrole-H), 6.20 (2H, m, pyrrole-H), 6.62 (2H, m, pyrrole-H), 7.82 (2H, bs, NH). FT-IR (cm<sup>-1</sup>; group): (3,400, N–H). Cyclopentyldipyrrole **5**: yield 69 %, mp: 117–119 °C. <sup>1</sup>HNMR (solvent: CDCl<sub>3</sub>; internal standard: TMS):  $\delta = 1.74$  (4H, m, -CH<sub>2</sub>-C), 2.20 (4H, m, -CH<sub>2</sub>-C), 5.98 (2H, m, pyrrole-H), 6.06 (2H, m, pyrrole-H), 6.60 (2H, m, pyrrole-H), 7.78 (1H, bs, NH). FT-IR (cm<sup>-1</sup>; group): (3,378, N–H).

Cyclohexyldipyrrole **6**: yield 67 %, mp: 106–108 °C [40]. <sup>1</sup>HNMR (solvent: CDCl<sub>3</sub>; internal standard: TMS):  $\delta = 1.50$  (6H, m,  $-CH_2$ -C), 2.20 (4H, m,  $-CH_2$ -C), 6.10 (2H, m, pyrrole-H), 6.22 (2H, m, pyrrole-H), 6.63 (2H, m, pyrrole-H), 7.78 (1H, bs, NH). FT-IR (cm<sup>-1</sup>; group): (3,400, N–H).

2-Hydroxycyclohexyldipyrrole **7**: yield 63 %, mp: 106–108 °C. <sup>1</sup>HNMR (solvent: CDCl<sub>3</sub>; internal standard: TMS):  $\delta = 1.60$  (9H, m, –CH<sub>2</sub>-C), 2.30 (2H, m, –CH<sub>2</sub>-C), 2.71 (1H, m, –CH<sub>2</sub>-C), 4.09 (1H, bs, cyclohexyl-OH), 6.07 (2H, m, pyrrole-H), 6.18 (2H, m, pyrrole-H), 6.74 (2H, m, pyrrole-H), 7.80 (1H, bs, NH). FT-IR (cm<sup>-1</sup>; group): (3,408, N–H).

*Meso*-methyl-*meso*-phenyl-2,2'-dipyrromethane **8**: yield 70 %, mp: 103–105 °C [39]. <sup>1</sup>HNMR (solvent: CDCl<sub>3</sub>; internal standard: TMS):  $\delta = 2.07$  (3H, s, CH<sub>3</sub>-C), 6.01 (2H, m, pyrrole-H), 6.21 (2H, m, pyrrole-H), 6.75 (2H, m, pyrrole-H), 7.27 (5H, m, PhH), 7.80 (2H, bs, NH). FT-IR (cm<sup>-1</sup>; group): (3,421, N–H).

*Meso*-methyl-*meso*-(4-methylphenyl)-2,2'-dipyrromethane **9**: yield 61 %, mp: 119–120 °C. <sup>1</sup>H NMR (solvent: CDCl<sub>3</sub>; internal standard: TMS):  $\delta = 2.04$  (3H, s, C**H**<sub>3</sub>-C), 2.48 (3H, s, **H**<sub>3</sub>C-Ar), 5.89 (2H, m, pyrrole-H), 6.26 (2H, m, pyrrole-H), 6.70 (2H, m, pyrrole-H), 7.09 (4H, m, Ph**H**), 7.86 (1H, bs, N**H**). FT-IR (cm<sup>-1</sup>; group): (3,410, N–H).

*Meso*-methyl-*meso*-(4-methoxybenzyl)-2,2'-dipyrromethane **10**: yield 51 %, mp: 117–118 °C. <sup>1</sup>HNMR (solvent: CDCl<sub>3</sub>; internal standard: TMS):  $\delta = 2.06$  (3H, s, C**H**<sub>3</sub>-C), 3.64 (2H, s, Ar-C**H**<sub>2</sub>-C), 3.70 (3H, s, **H**<sub>3</sub>CO-Ar), 5.62 (2H, m, pyrrole-H), 5.89 (2H, m, pyrrole-H), 6.61 (2H, m, pyrrole-H), 6.86 (2H, d, J = 6.4, Ph**H**<sup>m</sup>), 7.14 (2H, d, J = 6.5, Ph**H**<sup>o</sup>), 7.91(2H, bs, N**H**). FT-IR (cm<sup>-1</sup>; group): (3,410, N–H).

## Synthesis of gold nanoparticles

The synthesis of gold nanoparticles was achieved by the chemical reduction of HAuCl<sub>4</sub> in water medium with dipyrromethane without using any stabilizer. In a typical experiments, HAuCl<sub>4</sub>·3H<sub>2</sub>O (0.03 g, 0.08 mmol) was dissolved in deionized H<sub>2</sub>O (3 ml) and *meso*-methyl-*meso*-phenyl-2,2'-dipyrromethane **8** (0.047 g, 0.2 mmol) was slowly added. The suspension was magnetically stirred for 1 h. Finally, the gold nanoparticles were separated from water by precipitation under centrifuge at 10,000 rpm. The desorbed organic monomer were removed from Au

nanoparticles surface by washing several times using acetonitrile and dichloromethane.

## **Results and discussion**

Preparation of substituted dipyrromethanes

The reaction of pyrrole with different ketones in water in the presence of a catalytic amount of  $Fe(HSO_4)_3$  under reflux condition gave mainly the desired dipyrromethane with 50–70 % yields (Scheme 1).

To obtain the best reaction conditions for dipyrromethanes synthesis, the effects of different parameters like solvent and catalyst molar ratio were investigated on the reaction of pyrrole and acetophenone as a model reaction.

At first, the reaction was carried out in several solvents  $(H_2O, EtOH, CHCl_3, CH_2Cl_2 \text{ and } C_6H_6)$ . As shown in Table 1,  $H_2O$  is the best solvent for dipyrromethane synthesis.

The yield of dipyrromethane as a function of catalyst concentration is also shown in Table 1. The maximum yield of **8** is observed when 10 mol % molar ratio of catalyst is used. The yield decreases remarkably at higher concentration of catalyst (Table 1).

In our synthetic endeavor, we found out that pyrrole and ketones undergo condensation reaction in an aqueous medium by the drop-wise addition of  $Fe(HSO_4)_3$  solution at reflux condition. Different substituted dipyrromethanes are prepared in 50–70 % yields by this green method in aqueous conditions (Table 2).

It is proposed that the reaction occurs at the interface between the pyrrole and the aqueous ketone solution and the release of the product from the aqueous layer takes the reaction to completion and also prevents the reactions to proceed further [39].

Preparation and characterization of gold nanoparticles

There are many reports on the synthesis of gold nanoparticles in the presence of pyrrole and aniline [41–43]. When these monomer compounds are added to the solution, each nuclei serves as a catalytic reaction centre to enhance the reaction between  $AuCl_4^-$  ions and the monomers. These results suggested that autopolymerization of the monomers occurred on gold nanoparticles [41]. In other words,  $AuCl_4^-$  ions are reduced to form gold atoms and the



Scheme 1 Preparation of different substituted dipyrromethanes

**Table 1** Synthesis of meso-methyl-meso-phenyl-2,2'-dipyrrome-thane (8) using various conditions

Entry	Solvent	Catalyst:ketone	Yield (%) <sup>a</sup>
1	EtOH	0.1:1	60 %
2	$CH_2Cl_2$	0.1:1	40 %
3	CHCl <sub>3</sub>	0.1:1	20 %
4	C <sub>6</sub> H <sub>6</sub>	0.1:1	5 %
5	$H_2O$	0.1:1	70 %
6	$H_2O$	10:1	_ <sup>b</sup>
7	H <sub>2</sub> O	1:1	5 %
8	H <sub>2</sub> O	0.5:1	40 %

The reactions were performed with 1 mmol of acetophenone and 2 mmol pyrrole in solvent (5 ml) in the presence of (10 mol %) Fe(HSO<sub>4</sub>) under reflux condition

<sup>a</sup> Isolated yields

<sup>b</sup> TLC did not show dipyrromethane formation

organic compound oxidized simultaneously to produce polymers in situ.

On the other hand, dipyrromethanes are important precursors for the synthesis of *meso*-substituted porphyrins, corroles, and related compounds such as calixpyrroles macrocycles. In addition, for decades, a number of methods have been developed for the synthesis and purification of dipyrromethanes along with their oligomeric or polymeric by-products. So, these results demonstrate that polymerization of dipyrromethanes can occur in suitable conditions. Also, it is mentioned that there are some studies on electrochemical polymerization of dipyrromethanes and limited reports about their electrochromic properties [44].

So, in this present study, we introduce a facile route to synthesize gold nanoparticles using dipyrromethanes as reducing agents without the presence of any stabilizing or capping agents in large quantities, for the first time. For this purpose, we examined the application of three different substituted dipyrromethanes, meso-dimethyl-2,2'-dipyrromethane 1, meso-ethyl-meso-methyl-2,2'-dipyrromethane 3 and meso-methyl-meso-phenyl-2,2'-dipyrromethane 8, in the synthesis of gold nanoparticles. Gold nanoparticles exhibit strong plasmon resonance absorption that its  $\lambda_{max}$ depends on the particle size and the shape [45-47]. The characteristic UV-vis absorption spectra of the Au nanoparticles prepared by this method are shown in Fig. 1. The plasmon band of gold nanoparticles synthesized by dipyrromethanes 1, 3 and 8 is observed at 525, 542 and 535 nm, respectively. These results indicated that the reduction of AuCl<sub>4</sub><sup>-</sup> occurs by these three substituted dipyrromethanes to produce the gold nanoparticles.

The peak intensity and position of the surface plasmon absorption band are dependent on the size and shape of the metal nanoparticles, the dielectric constant of the metals as well as the medium surrounding the particles [48]. An



Ketone	Product (number)		yeild(%) <sup>a</sup>
0	H <sub>3</sub> C CH <sub>3</sub>		
H <sub>3</sub> C CH <sub>3</sub>		(1)	71%
O L	H <sub>3</sub> CH <sub>2</sub> C CH <sub>2</sub> CH <sub>3</sub>		
H <sub>3</sub> CH <sub>2</sub> C <sup>C</sup> CH <sub>2</sub> CH <sub>3</sub>		(2)	68%
O 	H <sub>3</sub> CH <sub>2</sub> C CH <sub>3</sub>		
H <sub>3</sub> CH <sub>2</sub> C CH <sub>3</sub>	NH HN	(3)	57%
H <sub>3</sub> C U CH <sub>3</sub>	(H <sub>3</sub> C) <sub>2</sub> HC CH(CH <sub>3</sub> ) <sub>2</sub>		
HC CH H <sub>3</sub> C CH <sub>3</sub>	NH HN	(4)	55%
O 	$\Box$		
$\bigcirc$	NH HN	(5)	69%
O 	$\bigcap$		
$\bigcirc$		(6)	67%
0			
ОН	OH		
$\smile$	NH HN	(7)	63%
O II			
CH <sub>3</sub>		(0)	70%
	H <sub>3</sub> C, NH HN	(8)	70%
O 			
CH <sub>3</sub>	CH <sub>3</sub>		010/
H <sub>3</sub> C	NH HN	(9)	61%
	n <sub>3</sub> CU		
CH <sub>3</sub>	CH <sub>3</sub>	(1.0)	= 10/
H <sub>3</sub> CO	NH HN	(10)	51%

The reactions were carried out in 1 mmol of acetophenone, 2 mmol pyrrole and Fe(HSO<sub>4</sub>)<sub>3</sub> (10 mol %) in water at reflux conditions <sup>a</sup> Islolated yields

intense absorption peak at 517 nm is generally attributed to the surface plasmon excitation of small spherical gold particles [49]. When the GNP size increases, the maximum extinction of surface plasmon band (SPB) is red shifted slightly in the visible region which may be attributed to the surface plasmon oscillation of free electrons. However, it can be affected by four factors: density of electrons, electron mass, mass and size of the charged nanoparticles.

On the other hand, when the shape of the nanoparticles changes from nanosphere to nanorods, the surface plasmon absorption spectrum also changes [50]. The surface plasmon absorption of gold nanorods have two bands: a strong long wavelength band in the near infrared region due to the



Fig. 1 UV-vis spectra of the as-prepared gold nanoparticles dispersed in water in the presence of dipyrromethanes 1, 3 and 8

longitudinal oscillation of electrons and a weak short wavelength band in the visible region around 520 nm due to the transverse electronic oscillation.

For further characterization of these prepared gold nanoparticles, we chose the product obtained from reagent 8.

Figure 2 shows the TEM image of gold nanoparticles prepared by this method in the presence of meso-methyl*meso*-phenyl-2.2'-dipyrromethane 8. The micrograph clearly indicates the formation of nanoparticles with an average diameter of 30 nm. The particles do not get selfassembled because the polymeric compound obtained from the oxidation of compound 8 acts as a capping agent.

Figure 3 shows typical SEM images of the resulting nanoparticles. The image indicates that the precipitates consist of a mass of plates coexisted with spherical particles. To the best of our knowledge, no previous work has



Fig. 2 Typical TEM image of individual gold nanoparticles in water medium. The scale bar is 50 nm



Electron Image 1

Fig. 3 Typical SEM images of the resulting precipitates of gold nanoparticles

been reported about the preparation of gold nanoparticles in the presence of dipyrromethane system.

The EDX spectrum determined from these purified nanoparticles shows strong peaks due to gold element. Weak peaks ascribed to carbon are also observed (Fig. 4), which reveals these gold nanoparticles are covered with oxidized dipyrromethane 8.

In order to confirm the formation of a crystal phase and calculate the mean size of the nanoparticles, X-ray diffraction (XRD) analysis was performed (Fig. 5). Figure 5 presented an XRD pattern of the gold nanoparticles after centrifugation. The labeled diffraction peaks appearing at  $2\theta = 38.35^{\circ}, 44.58^{\circ}, 64.74^{\circ}, 77.75^{\circ}$  and  $81.87^{\circ}$  corresponding to the (111), (200), (220), (311) and (222) planes of the standard cubic phase of Au, respectively, are similar to pure gold nanoparticles. The broad peak at about 28° can be associated with the amorphous form of the polymer which surrounded the gold nanoparticles [41, 51].

An overwhelming intensity diffraction peak located at 38.35 is attributed to the {111} facets of face-centered cubic (fcc) gold crystal (JCPDS no. 4-0783) while diffraction peaks of other four facets are weak. This confirms that the nanoparticles were mainly dominated by {111} facets, which were oriented parallel to the supporting surface preferentially.



Fig. 4 The EDX pattern of the purified gold nanoparticles





The crystallite size of gold nanoparticles  $(\tau)$  was deduced from XRD line broadening using the Scherrer equation:

 $\tau = K\lambda/\beta\cos\theta$ 

where *K* is a constant (0.94),  $\lambda$  is the X-ray wavelength (Cu  $K\lambda$ ,  $\lambda = 1.54184$  Å),  $\beta$  is the line broadening at half the maximum intensity (FWHM) in radians, and  $\theta$  is the half diffraction angle of the centroid of the peak in degrees. Contributions to broadening due to the non-uniform stress were neglected and the XRD instrumental line width was subtracted. The average size of the gold nanoparticles ranged from 30.1, 27.8 and 28.8 nm (mean 28.9 nm) for the (111), (200) and (220) planes, respectively, and hence was in good agreement with the UV–vis spectroscopy and TEM measurements. In other words, all obtained results are confirming and complement each other. The XRD data suggests that the nanoparticles are polycrystalline in nature with a predominant (111) Bragg reflection (Scheme 2).

According to thermodynamic points, gold atoms should nucleate and grow in a solution phase to form sphere like cuboctahedrons bounded by a mix of {111} and {100} facets. If the nucleation and growth of gold nanoparticles were subjected to kinetic control, gold atoms would preferentially add to facets of the seeds with higher surface energies. In the meantime, the oxidative products of dipyrromethane, including its polymers or oligomers, inclined to adsorbing on the lowest energy {111} facets of the particles and compress the growing rate of these facets. Then, as a result, other facets adsorbed with fewer molecules of oxidized dipyrromethane grew more quickly than {111} facets and polygonal gold plates bound primarily by {111} facets were preferentially generated. However, insufficient quantity of dipyrromethane also decreased the production of oxidized dipyrromethane, so that cannot effectively work as a capping agent for special facets. This finally resulted in dominating big quasi-spherical particles



Scheme 2 Schematic formation of gold nanoparticles with a predominant (111) Bragg reflection using dipyrromethane 8

rather than plates. Excessive quantity of dipyrromethane led to a high reduction rate of  $AuCl_4^-$  ions, leading to thermodynamic control over both nucleation and growth. This leads to a heavy coverage of oxidized dipyrromethane on the surfaces of the particles and results in products dominated by spherical particles due to the isotropic growth of all facets [52].

# Conclusions

In conclusion, we demonstrate a facile route to synthesize single-crystal, polygonal gold nanoparticles bounded mainly by {111} facets in aqueous solution using dipyrromethane as the reducing agent at room temperature without the presence of any stabilizing or capping agents in large quantities. During the synthetic process, the dipyrromethane acted as reducing agent and their oxidative products worked as capping agents to control the growing rate of different facets of the initial gold nuclei leading to the formation of the gold nanoparticles bound primarily by {111} facets. In this study, dipyrromethanes have been prepared from pyrrole and ketones in water and in the presence of ferric hydrogen sulfate, which is an inexpensive, non-toxic and environment friendly catalyst.

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