

# Analytical Methods

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3 **Reply to the 'Comment on "Simple fluorescence-based detection of Cr(III) and Cr(VI)**  
4 **using unmodified gold nanoparticles"' by M. R. Hormozi-Nezhad, J. Mohammadi and A.**  
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6 **Bigdeli, *Anal. Methods*, 2015, 7, DOI: 10.1039/c5ay00816#**  
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11 Sruthi Ann Alex, M. Elavarasi, D. Nanda Kumar, A. Rajeshwari, N. Chandrasekaran, and \*Amitava  
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3 We have keenly read the comment on our recent article by Hormozi-Nezhad et al. In our study,<sup>1</sup> AuNPs  
4 were synthesized using Turkevich method. The hydrodynamic size of the as-synthesized AuNPs  
5 was found to be 31.178 nm by dynamic light scattering analysis. According to several reports,<sup>2-6</sup>  
6 the fluorescence of unmodified AuNPs with particle size greater than 2 nm has been investigated  
7 for sensing applications and biomolecule interaction studies. The fluorescence of AuNPs has also  
8 been found to be dependent on the size and zeta potential of the nanoparticles.<sup>7-9</sup> In addition,  
9 Förster resonance energy transfer (FRET)-based detection strategies have also been attempted by  
10 Hormozi-Nezhad et al. themselves, wherein the energy transfer between AuNPs (particle size > 10  
11 nm) and fluorescein isothiocyanate was analyzed for the detection of captopril.<sup>10</sup> FRET is a  
12 phenomenon that takes place between two fluorophores which are in close proximity,<sup>11</sup> and  
13 hence, these reports have also exploited the inherent fluorescence of gold nanoparticles, thus  
14 highlighting the fact that the AuNPs synthesized by the current method<sup>1</sup> also possesses inherent  
15 fluorescence despite having a particle size of 31.178 nm.  
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35 Rayleigh scattering peak is generally centered where the emission is equal to (or twice that of  
36 excitation in the case of second-order Rayleigh scattering) excitation. Rayleigh scattering of  
37 AuNPs can be minimized by altering the instrument parameters in the fluorescence  
38 spectrophotometer.<sup>12, 13</sup> The excitation and emission wavelength obtained in the study were 490  
39 nm and 582 nm, respectively, which shows that the emission observed was not equal to or twice  
40 that of the excitation wavelength being used. Figure 1 shows the excitation spectra of AuNPs  
41 before and after interaction with different concentrations of Cr(III) [ $10^{-6}$ – $10^{-3}$  M], which was  
42 recorded from 200 to 550 nm. Hence, the observed phenomenon is the actual fluorescence and  
43 was not obtained by the Rayleigh scattering of the incident light. On interaction of these AuNPs  
44 with Cr(III), the fluorescence measurements were taken immediately. The aggregation of AuNPs  
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3 occurs by the complexation of the citrate capping on AuNPs by Cr(III) ions.<sup>14</sup> The aggregation of  
4 AuNPs was found to be maximum at pH 3 when compared to the other observed pH as observed  
5 from our previous work.<sup>1,15</sup> Complexation of AuNPs causes color change<sup>1</sup> and peak shift in the  
6 spectral peak of AuNPs<sup>15</sup> as indicated in our previous works, and no precipitates were observed  
7 in the solution. If precipitation had occurred when the measurements were taken, the main peak  
8 of AuNPs would decrease drastically without prominent shift in the secondary peak, and the  
9 solution will start to turn colorless. Hence, the decrease in luminescence noticed was not due the  
10 precipitation of AuNPs. The concentration-dependent fluorescence signal decrease (emission  
11 spectra from 500 to 700 nm) observed at the optimized condition after Cr(III) interaction [ $10^{-6}$ –  
12  $10^{-3}$  M] could be repeated as observed from Figure 2. This reduction in the intensity could  
13 possibly be due to the AuNP aggregation<sup>15</sup> and the corresponding decrease in the absorbance of  
14 AuNPs just at the working excitation wavelength of 490 nm (Figure 1).  
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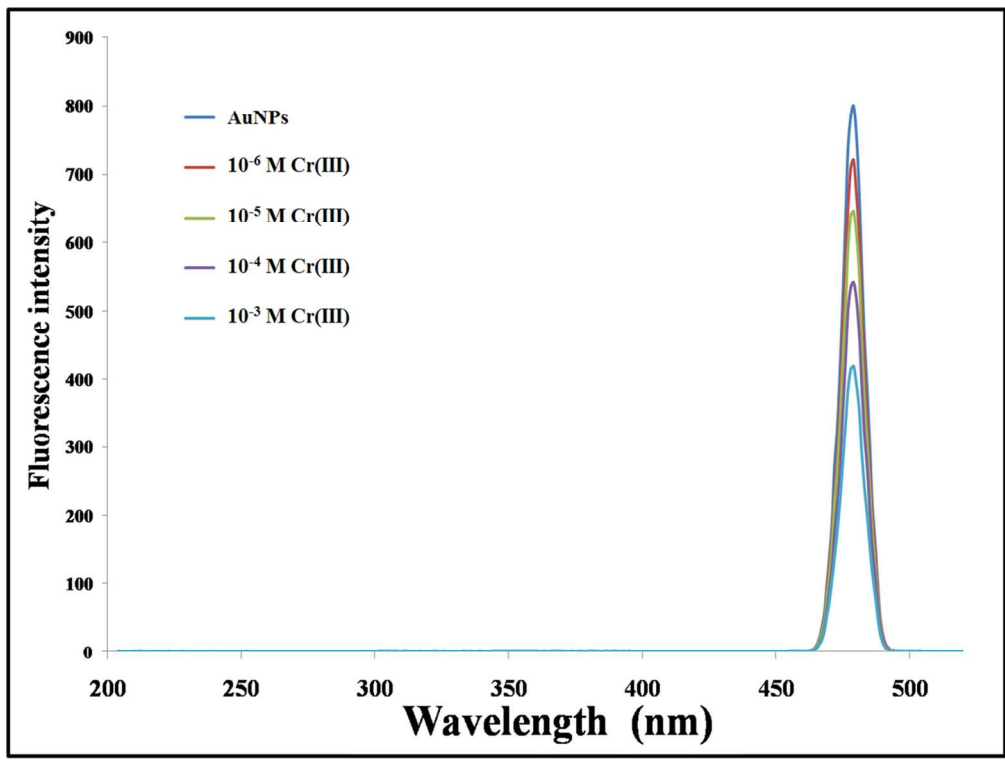
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### 33 34 **List of figures**

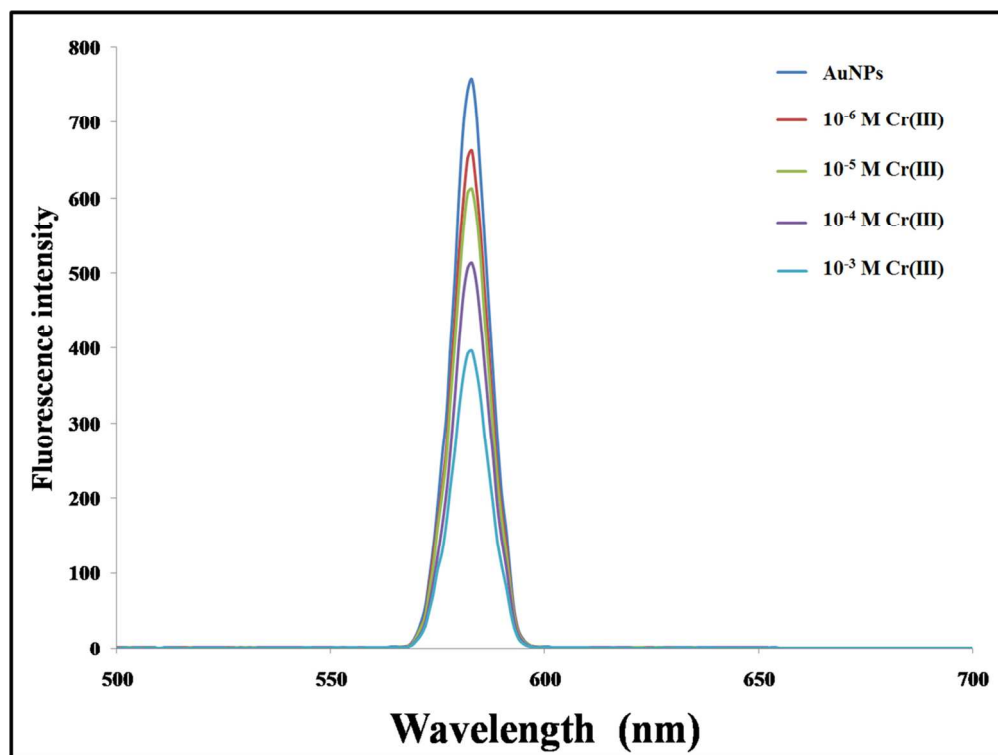
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36 **Figure 1** Excitation spectra of AuNPs in absence and presence of different concentrations of  
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38 Cr(III) [ $10^{-6}$ – $10^{-3}$  M] in the range 200–550 nm.  
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41 **Figure 2** Emission spectra of AuNPs in absence and presence of different concentrations of  
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43 Cr(III) [ $10^{-6}$ – $10^{-3}$  M] in the range 500–700 nm.  
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