# Analytical Methods

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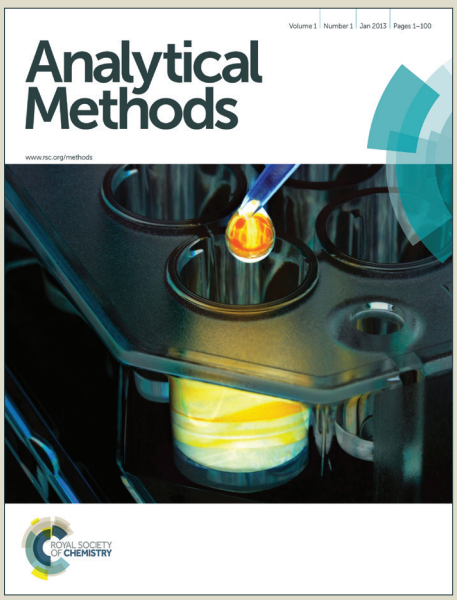





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# Reply to the 'Comment on "Simple fluorescence-based detection of Cr(III) and Cr(VI) using unmodified gold nanoparticles"' by M. R. Hormozi-Nezhad, J. Mohammadi and A. Bigdeli, *Anal. Methods*, 2015, 7, DOI: 10.1039/c5ay00816#

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We have keenly read the comment on our recent article by Hormozi-Nezhad et al. In our study,[1] AuNPs were synthesized using Turkevich method. The hydrodynamic size of the as-synthesized AuNPs was found to be 31.178 nm by dynamic light scattering analysis. According to several reports,[2-6] the fluorescence of unmodified AuNPs with particle size greater than 2 nm has been investigated for sensing applications and biomolecule interaction studies. The fluorescence of AuNPs has also been found to be dependent on the size and zeta potential of the nanoparticles.[7-9] In addition, Förster resonance energy transfer (FRET)-based detection strategies have also been attempted by Hormozi-Nezhad et al. themselves, wherein the energy transfer between AuNPs (particle size > 10 nm) and fluorescein isothiocyanate was analyzed for the detection of captopril.[10] FRET is a phenomenon that takes place between two fluorophores which are in close proximity,[11] and hence, these reports have also exploited the inherent fluorescence of gold nanoparticles, thus highlighting the fact that the AuNPs synthesized by the current method[1] also possesses inherent fluorescence despite having a particle size of 31.178 nm.

Rayleigh scattering peak is generally centered where the emission is equal to (or twice that of excitation in the case of second-order Rayleigh scattering) excitation. Rayleigh scattering of AuNPs can be minimized by altering the instrument parameters in the fluorescence spectrophotometer.[12, 13] The excitation and emission wavelength obtained in the study were 490 nm and 582 nm, respectively, which shows that the emission observed was not equal to or twice that of the excitation wavelength being used. Figure 1 shows the excitation spectra of AuNPs before and after interaction with different concentrations of Cr(III) [$10^{-6}$–$10^{-3}$ M], which was recorded from 200 to 550 nm. Hence, the observed phenomenon is the actual fluorescence and was not obtained by the Rayleigh scattering of the incident light. On interaction of these AuNPs with Cr(III), the fluorescence measurements were taken immediately. The aggregation of AuNPs

occurs by the complexation of the citrate capping on AuNPs by Cr(III) ions.[14] The aggregation of AuNPs was found to be maximum at pH 3 when compared to the other observed pH as observed from our previous work.[1,15] Complexation of AuNPs causes color change[1]and peak shift in the spectral peak of AuNPs[15] as indicated in our previous works, and no precipitates were observed in the solution. If precipitation had occurred when the measurements were taken, the main peak of AuNPs would decrease drastically without prominent shift in the secondary peak, and the solution will start to turn colorless. Hence, the decrease in luminescence noticed was not due the precipitation of AuNPs. The concentration-dependent fluorescence signal decrease (emission spectra from 500 to 700 nm) observed at the optimized condition after Cr(III) interaction [$10^{-6}$–$10^{-3}$ M] could be repeated as observed from Figure 2. This reduction in the intensity could possibly be due to the AuNP aggregation[15] and the corresponding decrease in the absorbance of AuNPs just at the working excitation wavelength of 490 nm (Figure 1).

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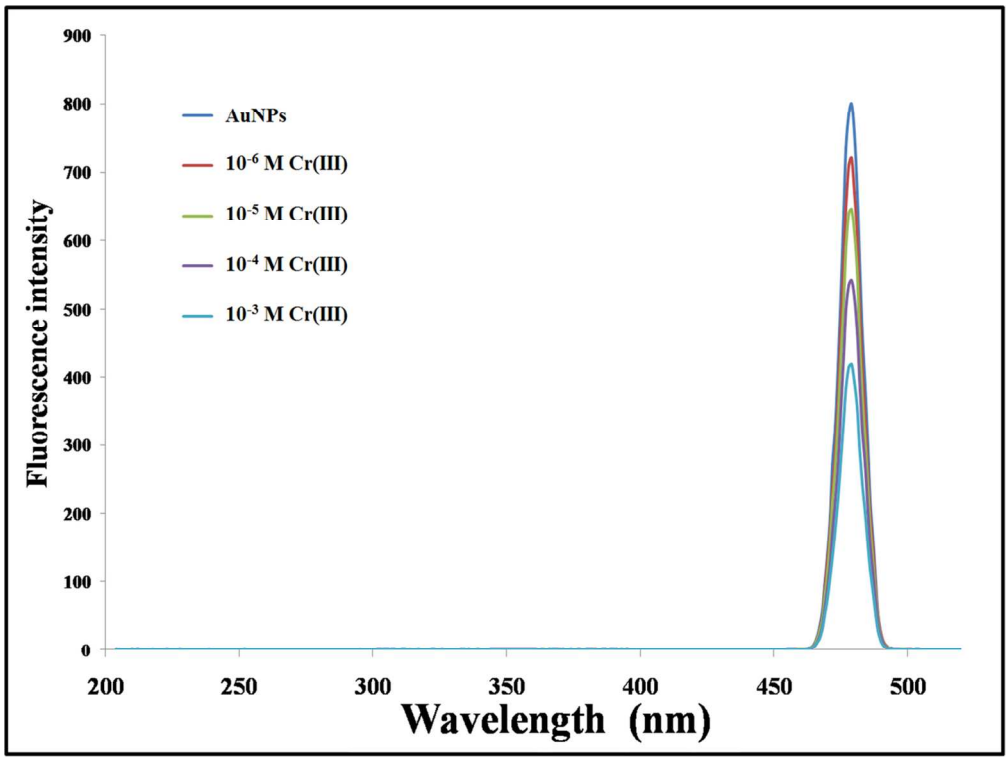
**Figure 1** Excitation spectra of AuNPs in absence and presence of different concentrations of Cr(III) [$10^{-6}$–$10^{-3}$ M] in the range 200–550 nm.

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

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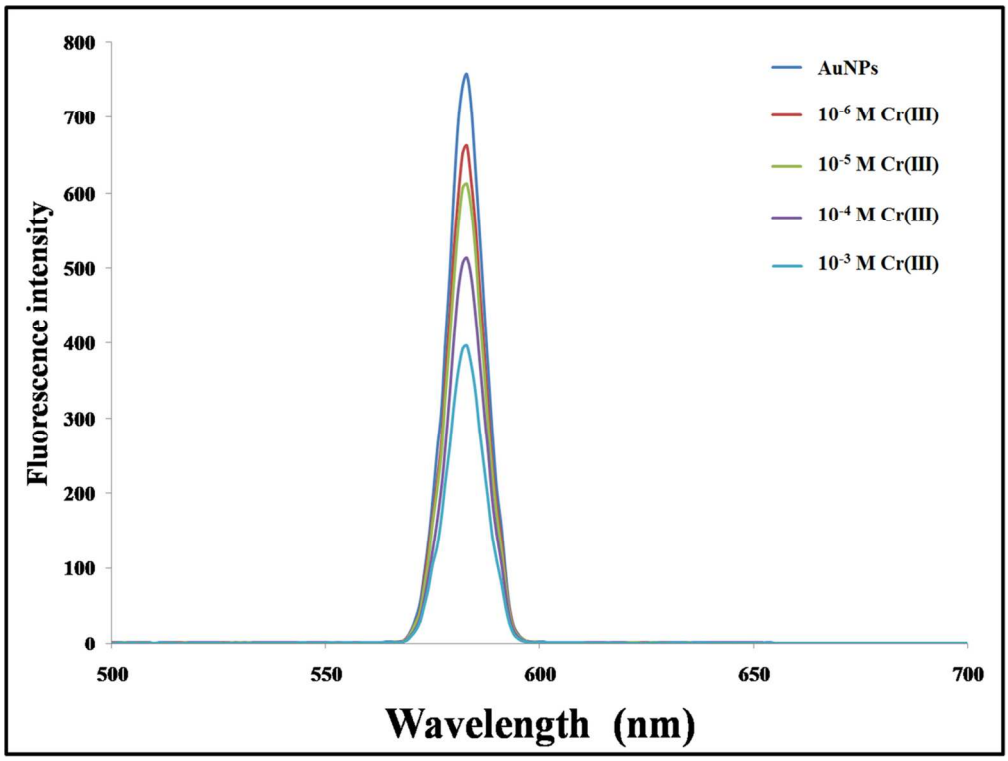


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