Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Structure and Dynamics of Gold Nanoparticles Decorated with Chitosan-Gentamicin Conjugates: ReaxFF Molecular Dynamics Simulations to disclose Drug Delivery

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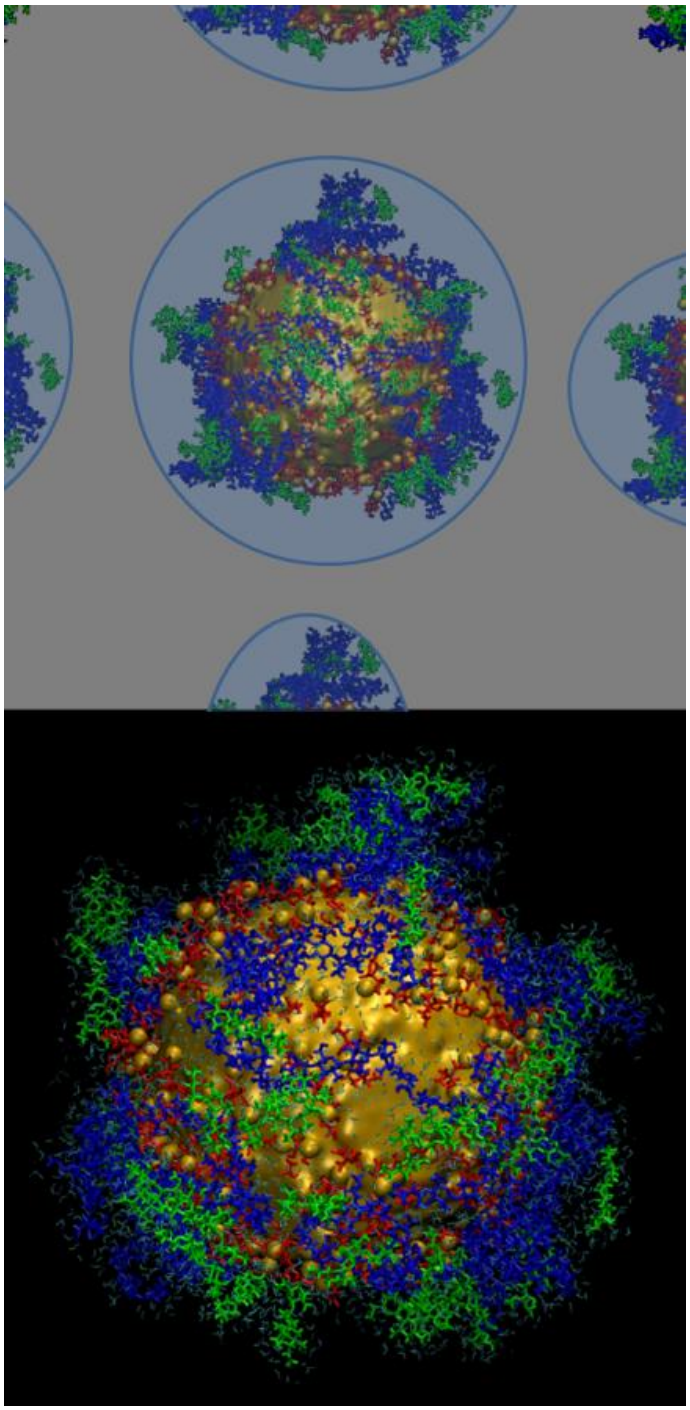


Figure S1. *(**Bottom**) Stabilized configuration of **CG-CIT-AuNP** in water solution (most of the water molecules are undisplayed for clarity and only a thin layer surrounding all the molecules and the AuNP is shown). (**Top**). Periodic images are shown to give an idea of the mutual positions of the NPs, which match fairly well the TEM images shown in the main text. All of the molecules are rendered with red, blue and green sticks that correspond to CIT, CHIT and GENT, respectively. Water molecules are displayed as cyan lines, whereas the AuNP by means of yellow-gold spheres, which are atoms escaped from the interface, and its solvent accessible surface.*

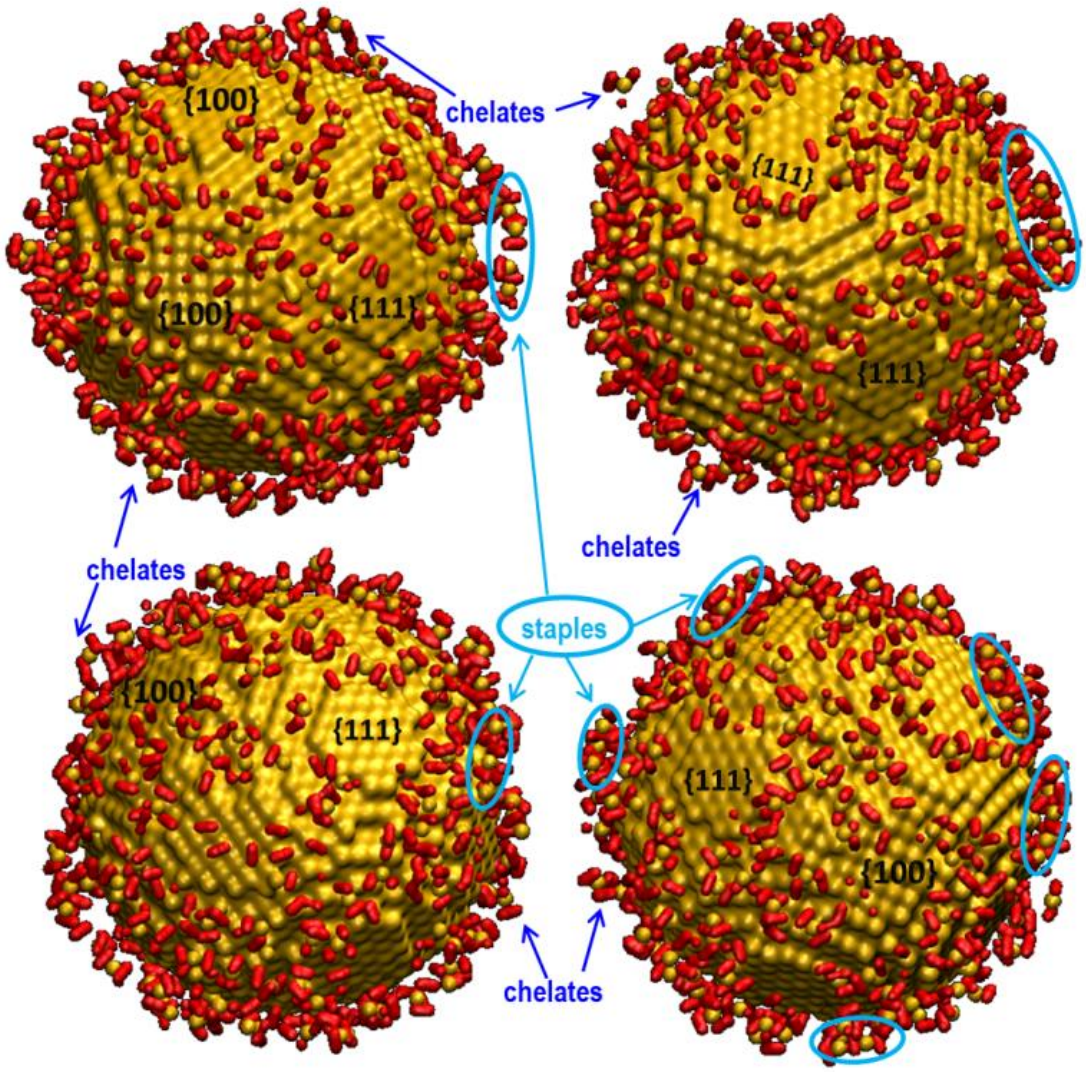


Figure S2. *Four different views of a stable configuration of* ***CG-CIT-AuNP*** *in water solution, where the CHIT chains, GENT molecules and water have been removed for clarity. Only the oxygens of the adsorbed CITs are shown as small red "capsules" (carboxyl groups) and spheres (hydroxyl oxygen). The AuNP is rendered by means of yellow-gold spheres (atoms escaped from the interface) and its solvent accessible surface. Some of the chelated structures and staple motifs (aligned molecules connected by gold atoms) are indicated by arrows and ellipses. The tendency of CIT to border the less reactive facets, adsorb on the face edges, and form a sort of chains (aligned configurations) is clearly shown.*

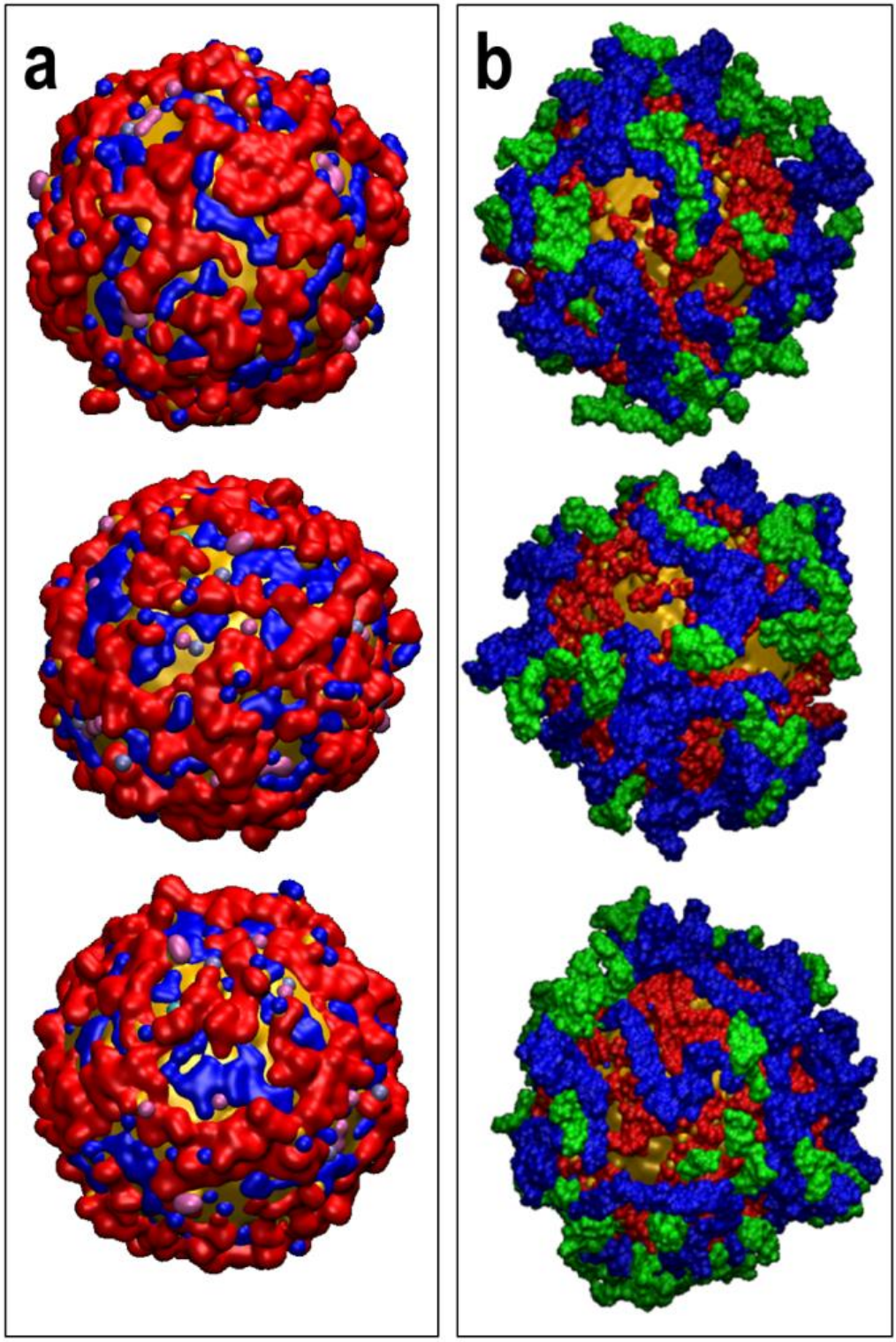
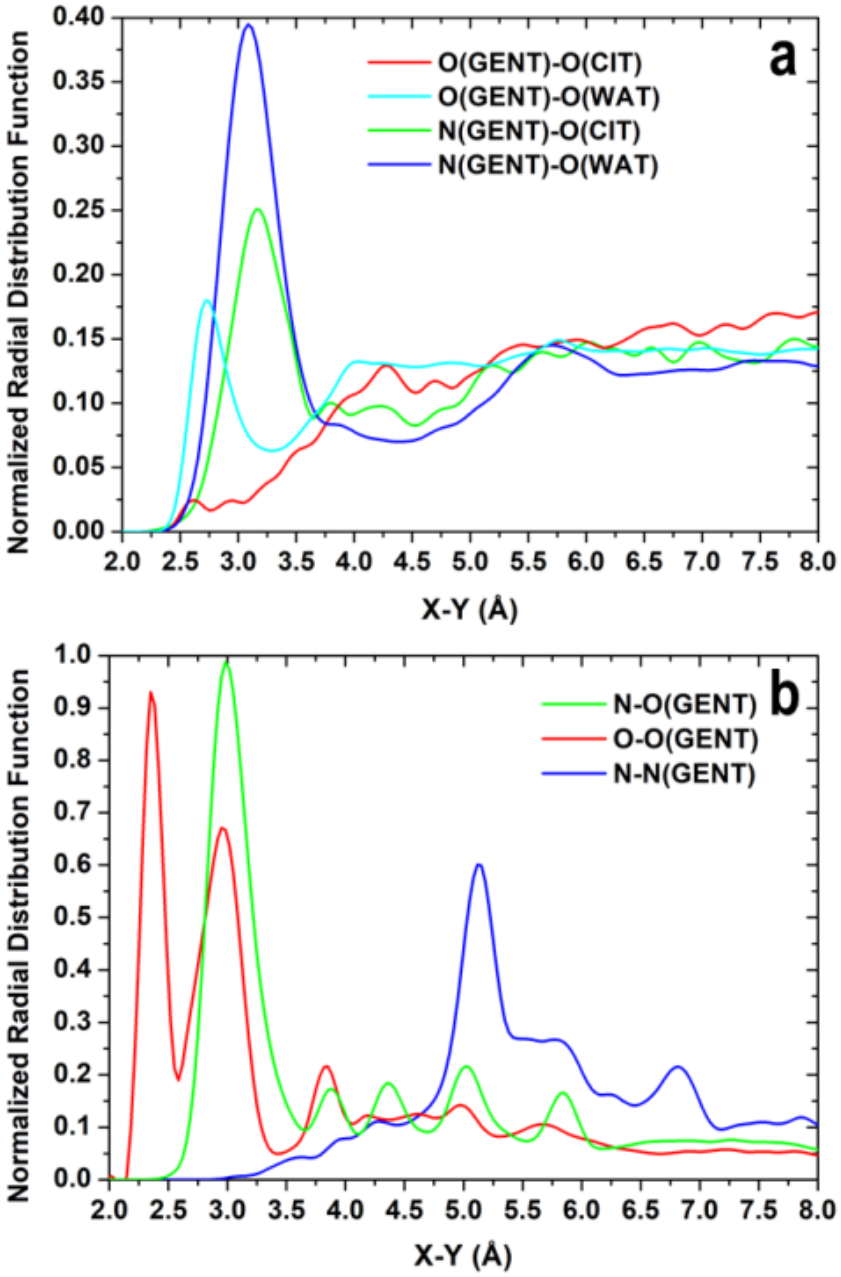


Figure S3. *Three different views of a stable configuration of* ***CG-CIT-AuNP*** *in water solution. (**a**) Distribution of the various molecules (rendered through their solvent accessible surfaces) within 3.5 Å of the interface: the adsorbed water is blue, CHIT groups in contact with gold are magenta, GENT groups in contact with gold are light violet-blue and adsorbed CIT groups are red; (b) the whole coating multilayer (without water) is visible: CIT red, CHIT blue and GENT green.*



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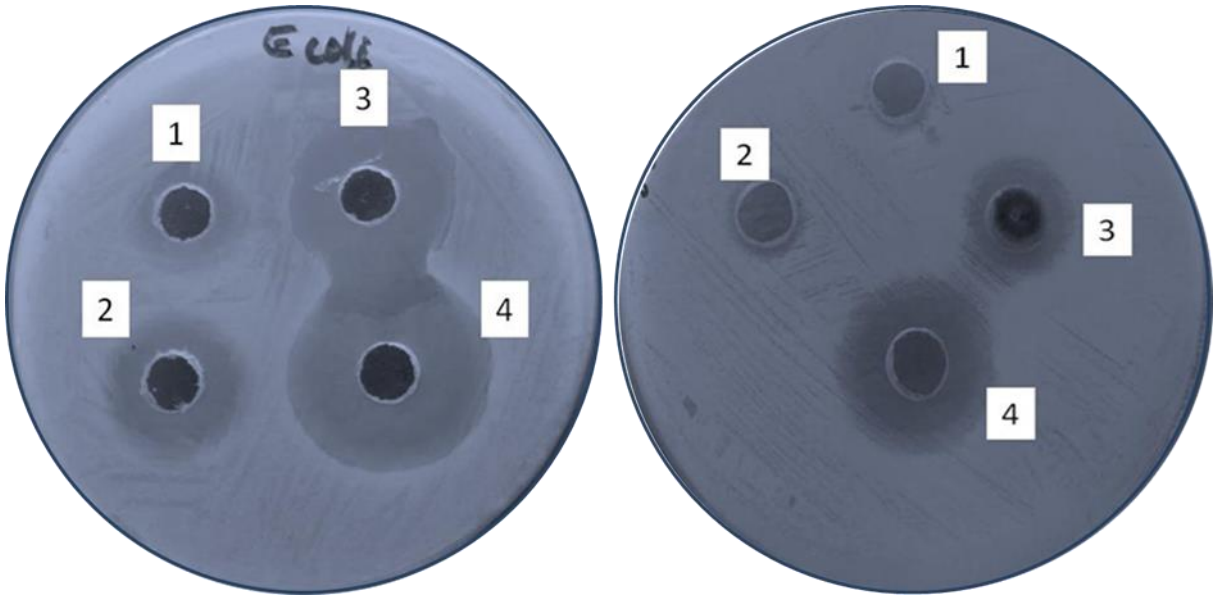

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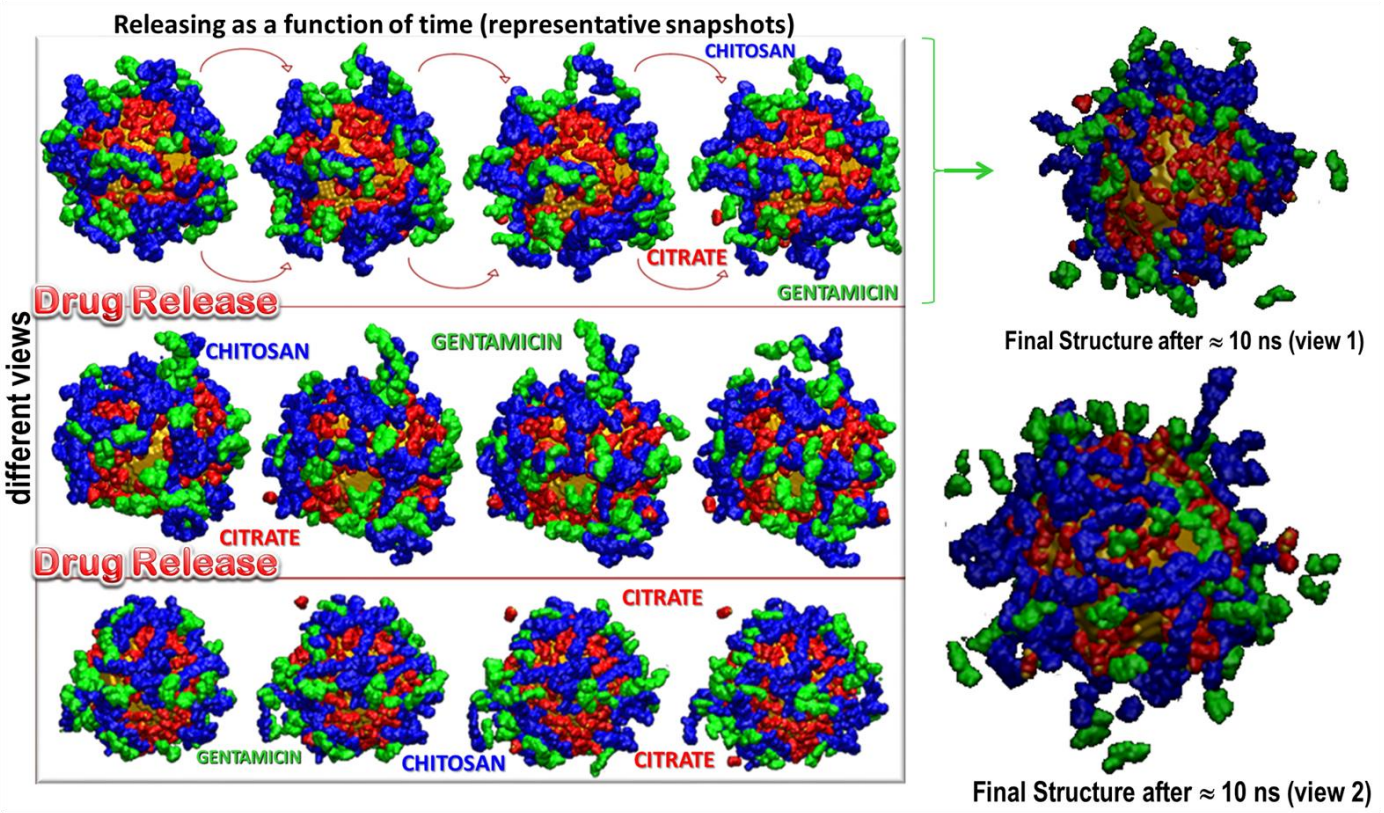

Figure S6. *Gentamicin Release induced by high temperature MD simulations.*

Short ReaxFF description

ReaxFF [van Duin, A. C. T.; Dasgupta, S.; et al., *J. Phys. Chem. A* **105**, 9396–9409 (2001)] is a general bond-order-dependent potential based on the bond distance/bond order and bond order/bond energy relationships for describing bond breaking and formation. Such a formulation, , is used effectively not only to represent appropriately under/over-coordination but also to exclude from the whole energy formulation the components which are no longer active upon bond breaking such as bond and dihedral angles terms. ReaxFF is a central force field where non-bonded interactions (Coulomb and van der Waals forces) are calculated between every atom pair. Shielding terms [Janssens, G. O. A.; Baekelandt, B. G.; et al., *J. Phys. Chem.* **99**, 3251–3258 (1995)] are used to dampen close range interactions and atomic charges are calculated using the electronegativity equalization method (EEM) developed by Mortier et al.[Mortier, W. J.; Ghosh, S. K.; et al., *J. Am. Chem. Soc.* **108**, 4315–4320 (1986)] and long-range Coulomb interactions are calculated by means of seventh-order taper function with an outer cutoff radius (usually of 10 Å).
The system energy in ReaxFF is calculated as the sum of a number of energy terms:

$$E_{system} = E_{bond} + E_{lp} + E_{over} + E_{under} + E_{val} + E_{pen} + E_{coa} + E_{C2} + E_{triple} + E_{tors} + E_{conj} + E_{H\text{-}bond} + E_{vdWaals} + E_{Coulomb}$$

The force field parameters are optimized against quantum chemistry data of model systems. These data can consist of atomic charges, bond lengths, bond angles, dihedral angles, lattice constants, heats of formations, reaction energies, and other descriptors that are usually weighted according to their importance. All the details regarding the program and its formulation can be found in the manual (https://www.scm.com/doc/ReaxFF/index.html) and in the references cited therein.

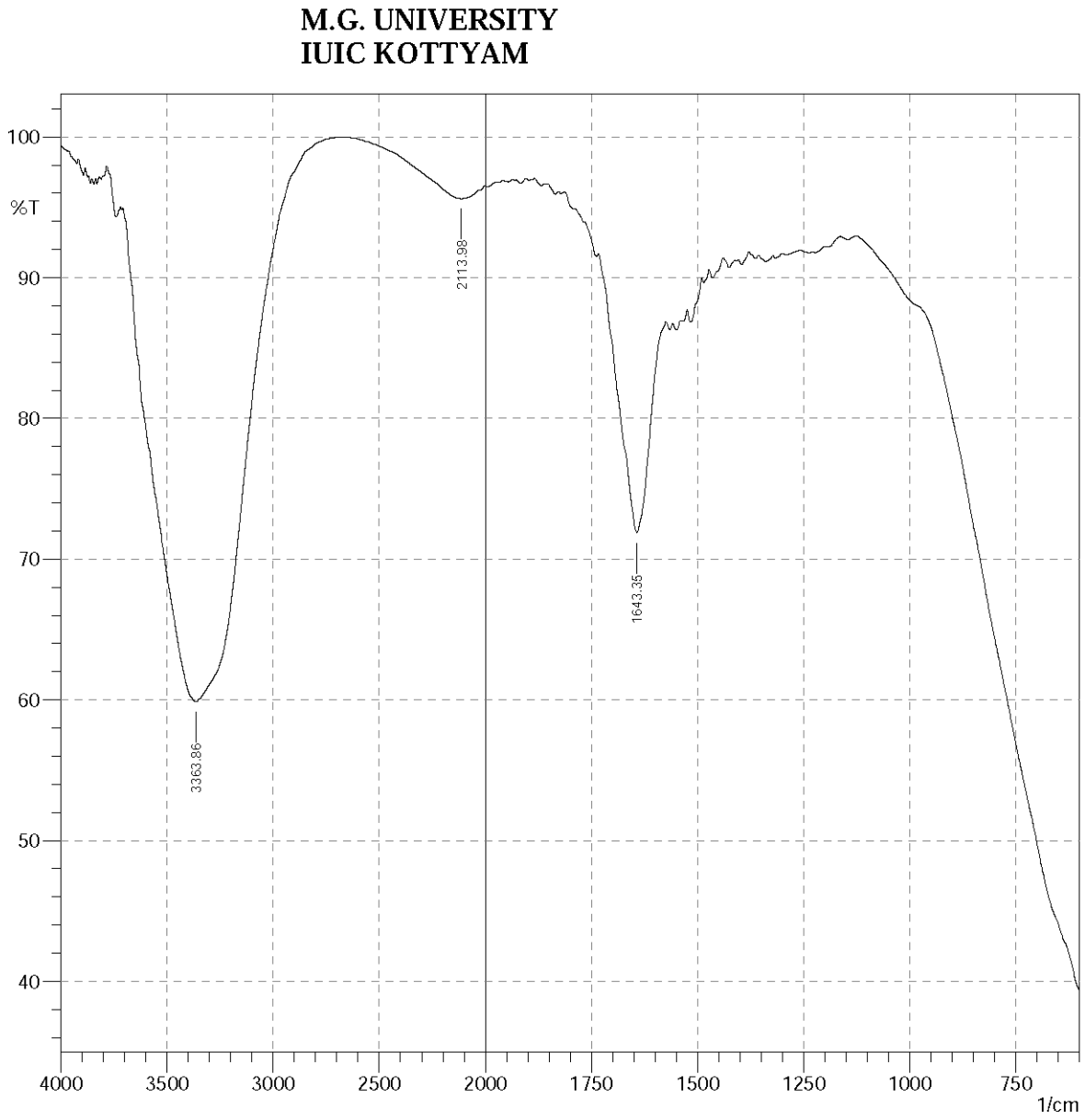

Figure S7. FTIR spectrum of CIT-AuNPs

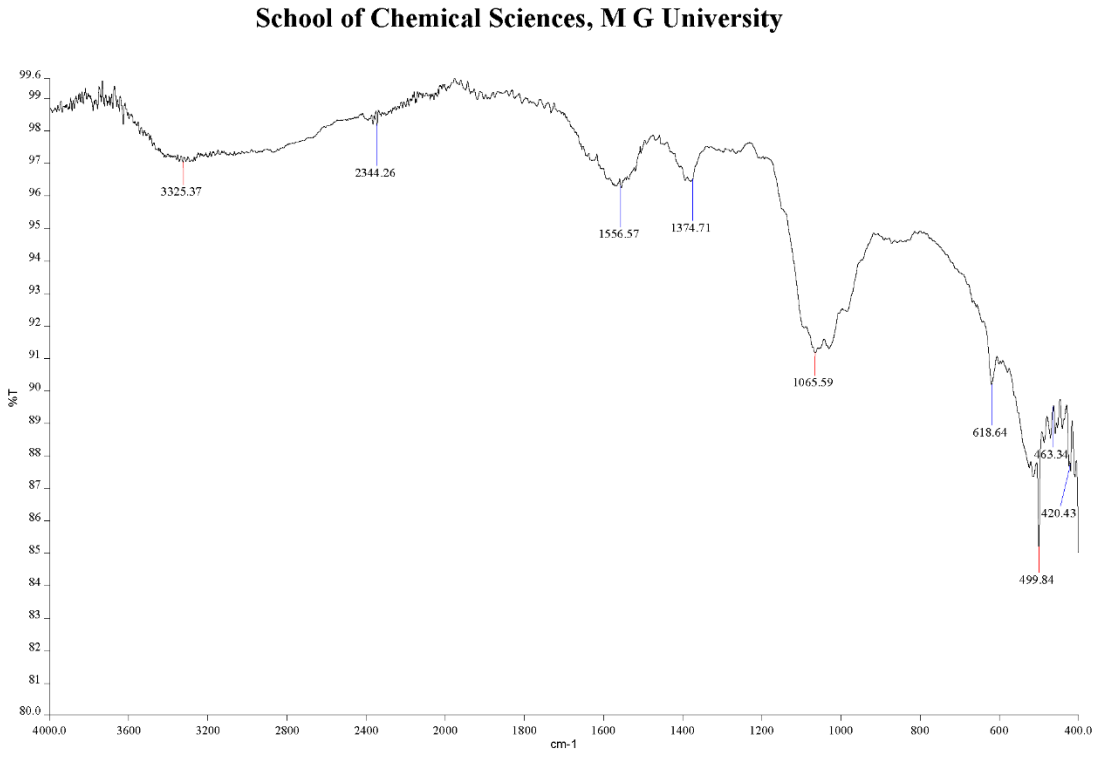

Figure S8. FTIR spectrum of CG-CIT-AuNPs