Supporting Information

Photoluminescent Graphene Nanoparticles for Cancer Photo-Therapy and Imaging

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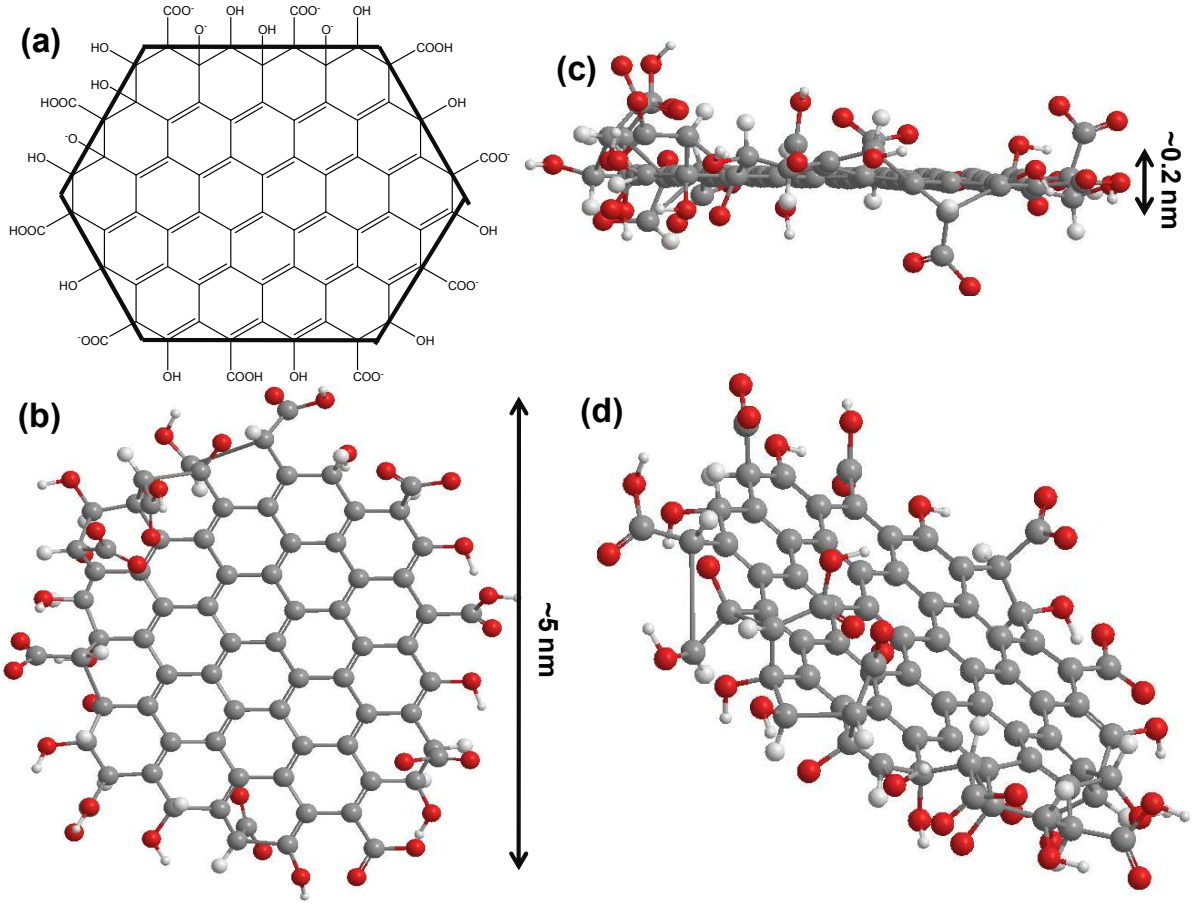

Figure S1. (a) 2D chemical structure of suspected cGdots. Proposed chemical structure of cGdots containing carbon (gray ball), hydrogen (white ball) and oxygen (red ball) with zigzag and armchair shaped (b) top view c) side view and d) angle view shows. The 2D structure shows a hexagonal shaped of cGdots containing functional groups on the edges where as the 3D structure show partially shrinkage of edge. The reason of this shrinkage is interaction among the functional groups.

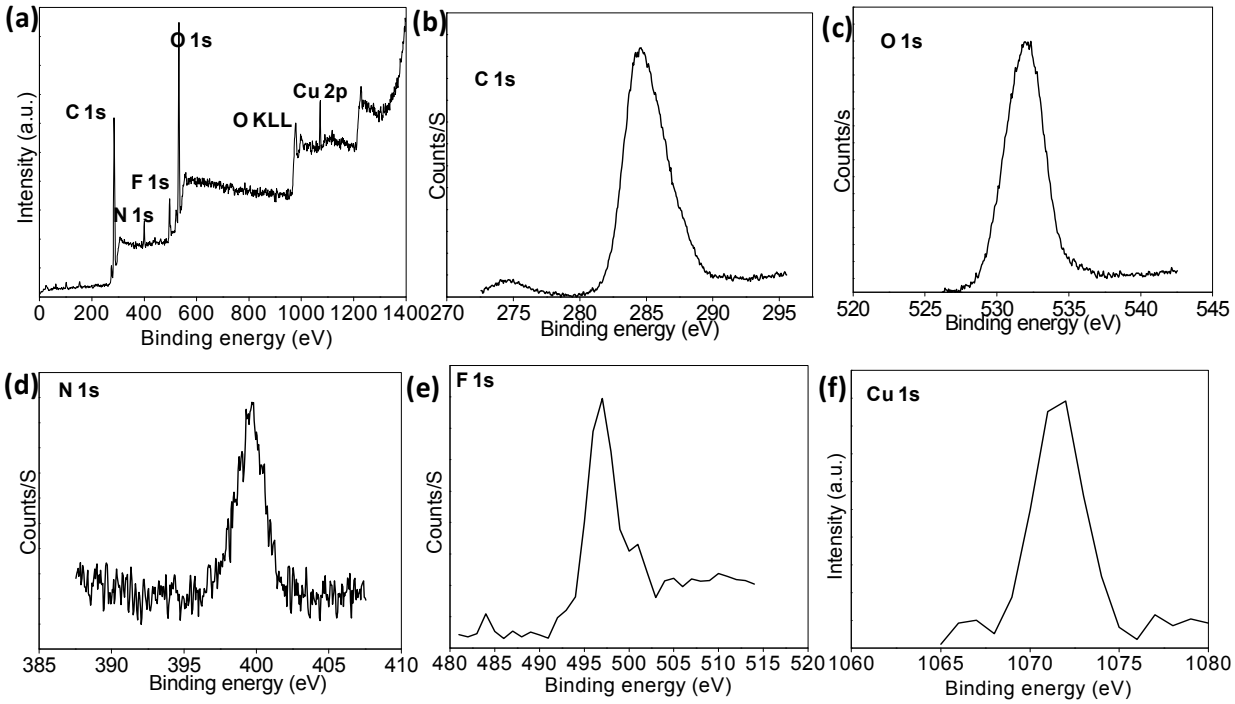

Figure S2. XPS spectrum of cGdots. A) XPS survey spectrum. High resolution spectrum of b) C 1s, c) O 1s, d) N 1s, e) F 1s and f) Cu1s. The Cu signal was from the substrate (Cu film).The chemical structure of cGdots was constructed based on XPS survey results (figure S2) and photoluminescence profile.

Table S1. Atomic content calculated from the XPS survey spectrums.

Elements	C	O	N	F	Cu
Content (%)	62.4	35.5	0.3	0.7	1.1

X-ray photoelectron spectroscopy (XPS) survey spectrum of cGdots shows carbon, oxygen, nitrogen, flurine and Cupper signals, shown in figure S5 a-f. The peaks at around 284.5, 533.5, 399.4, 496.4 and 1072.3 eV correspond to the C1s, O1s, N1s, F1s and Cu1s, respectively. The atomic content of cGdots is summarized in table S1. According to the table S1, the cGdots is mainly composed of carbon (62.4%), oxygen (35.5%) and very negligible amount of nitrogen (0.3%), flurine (0.7%) and cupper (1.1%) were considered as impurities during construct the chemical structure of cGdots. The Cu signal was from the substrate (Cu film).

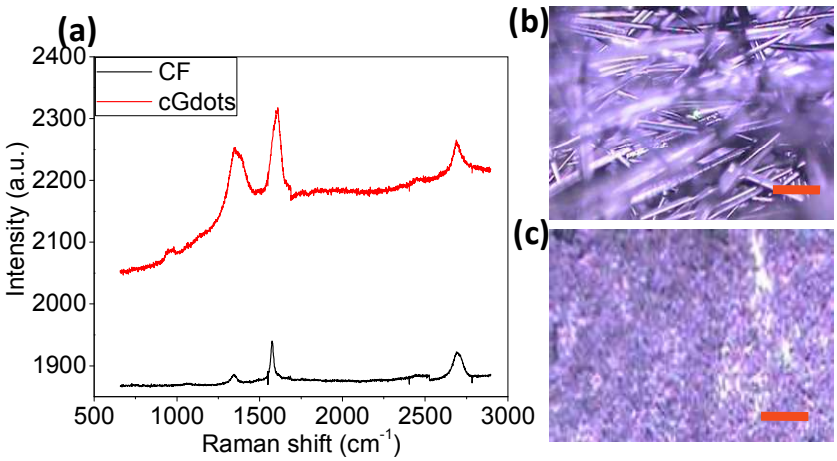

Figure S3. (a)Raman spectra of CF and cGdots, (b) observation of morphology of CF (scale bar=2 μm) and (c) cGdots (scale bar: 100 nm) by microscope.

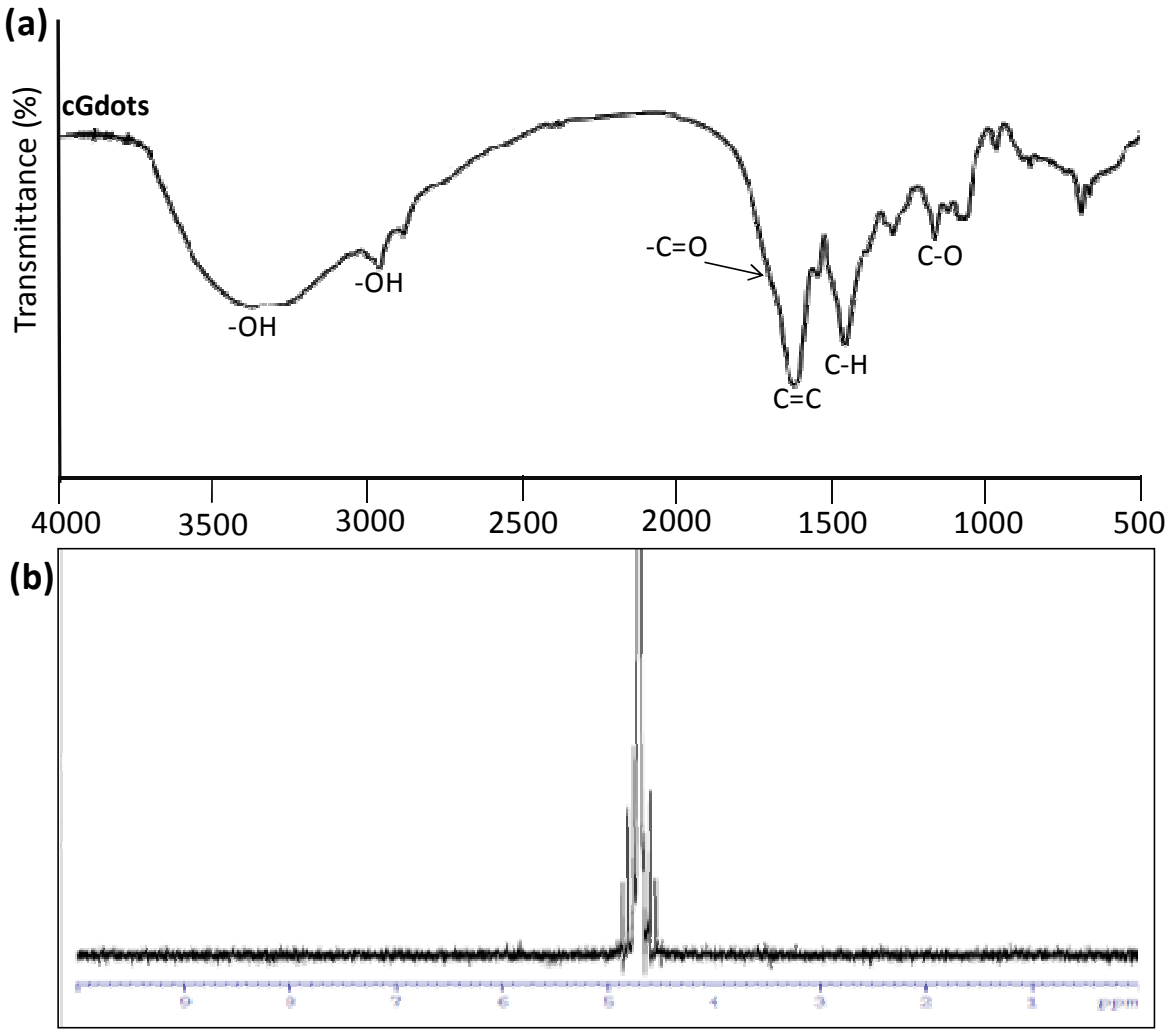

Figure S4. a) FT-IT spectrum and b) H-NMR of analysis data of as synthesized cGdots. FTIR spectrum of carbon fiber shows a straight line as it does not contains any functional groups Oxygen containing functional groups such as carbonyl, carboxyl and hydroxyl groups were introduce to the edges of the monolayer graphene as shown in the FTIR spectrum.

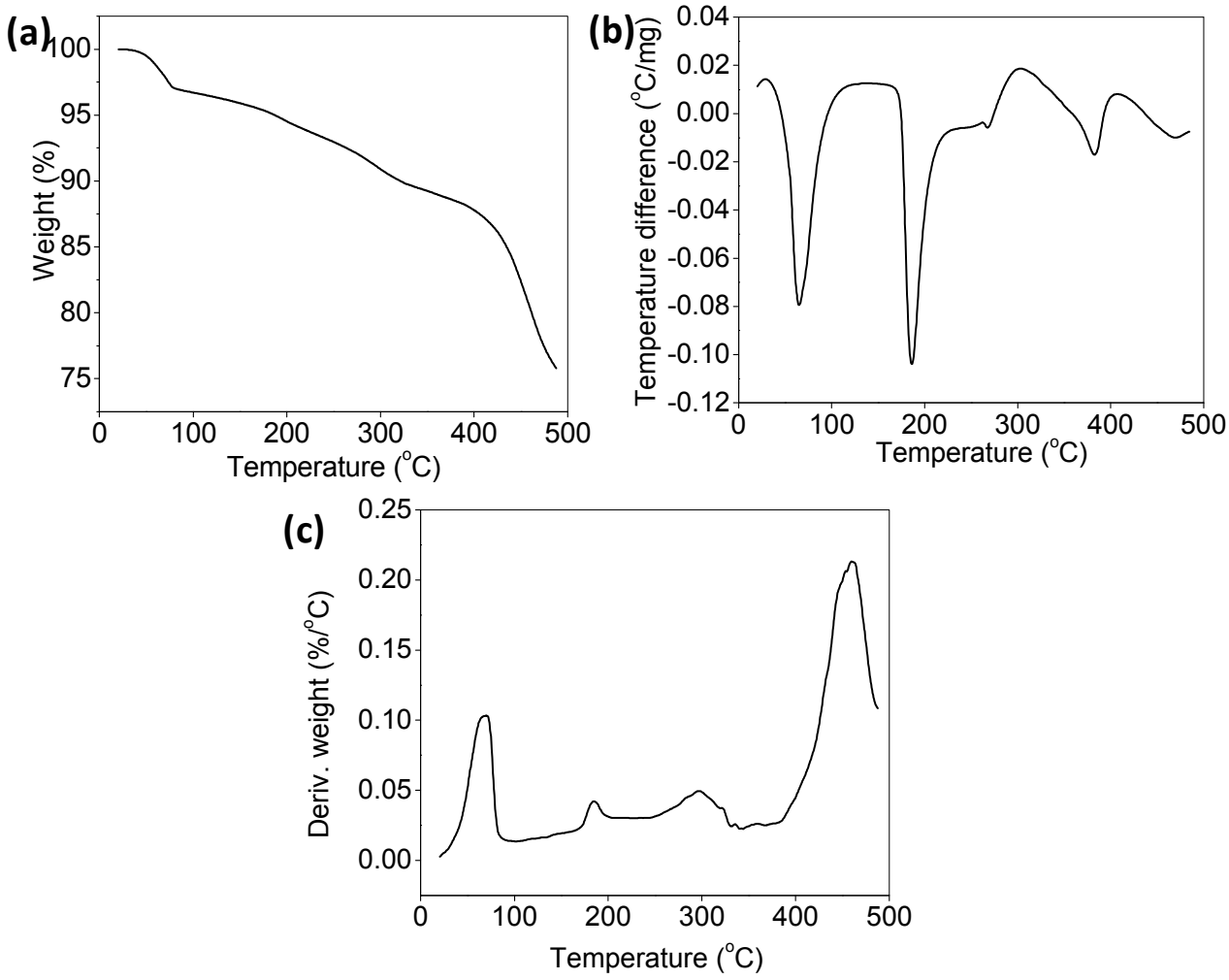

Figure S5. Thermal properties of cGdots, measured by a) TGA and b) DTA and c) TG shows weight loss with temperature, exo/endothermic profile and glass transition temperature of cGdots at different temperature. (Observation was done from 30 to 500 ^{o}C at 15 ^{o}C/min in nitrogen environment).

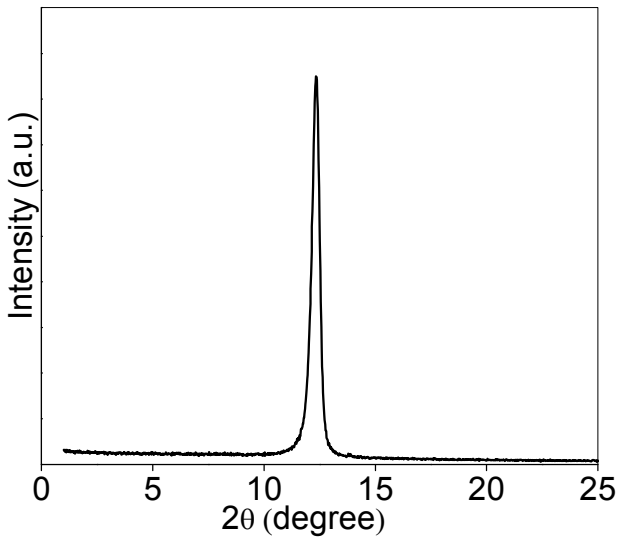

Figure S6. Physical properties of cGdots. XRD spectrum of cGdots shows 2θ value is 12.

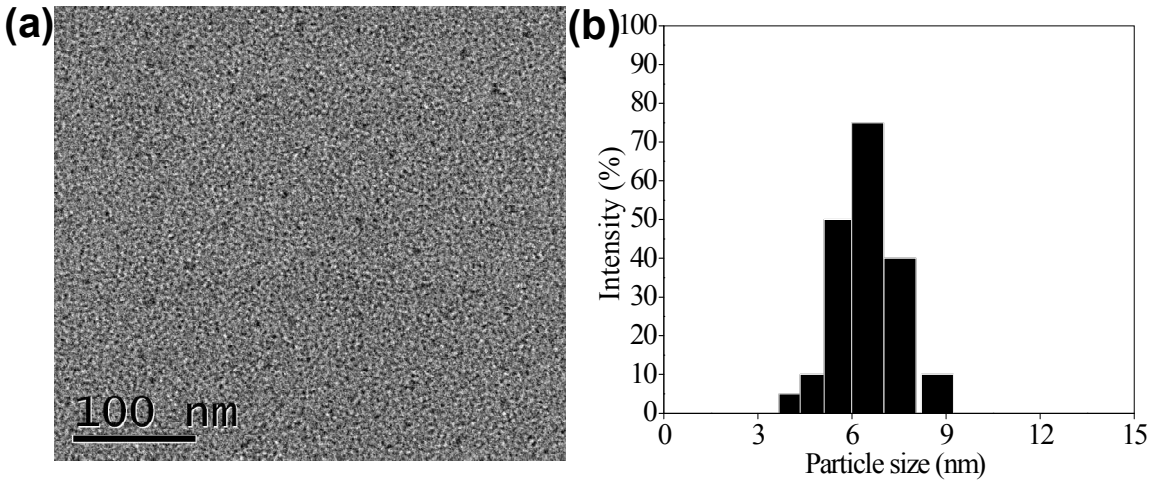

Figure S7. Size and morphology. a) Morphology and b) dynamic size of cGdots was measured by TEM and DLS, respectively.

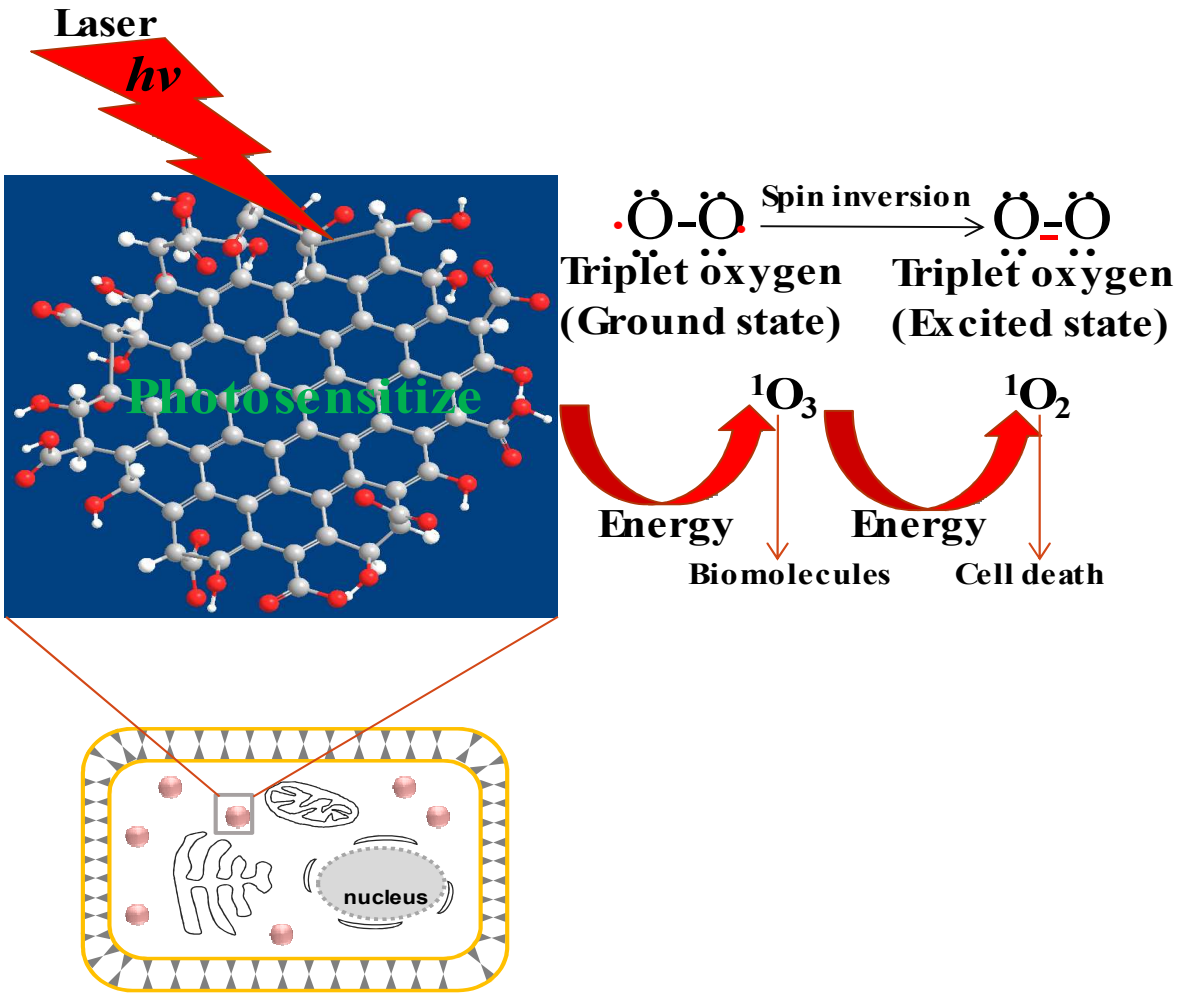

Figure S8. Mechanism of singlet oxygen generation from triplet oxygen through energy transfer from excited cGdots upon laser irradiation.

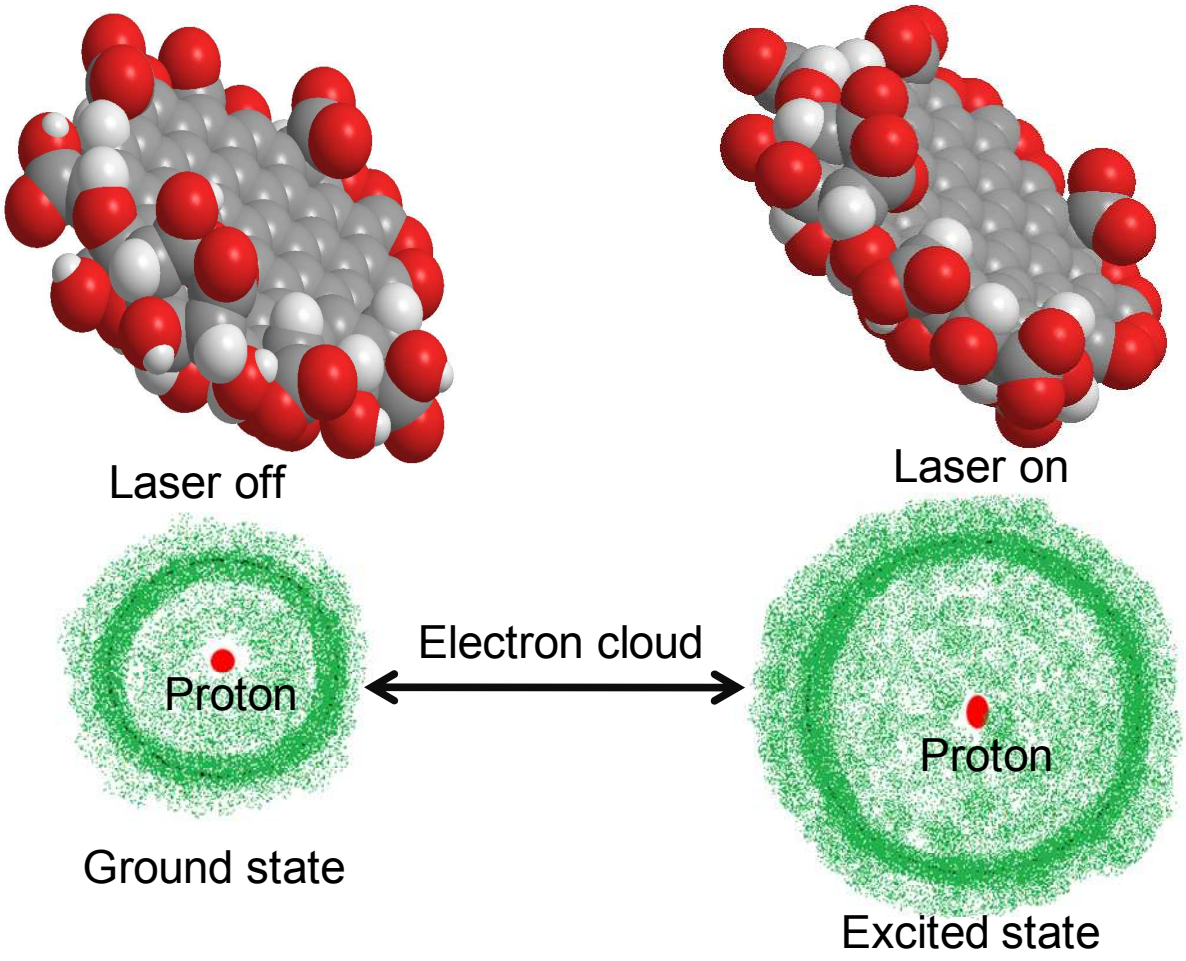

Figure S9. The model for ossilaration of electron cloud based on laser on/off shows the ground state electron become excited when the laser source on or active.

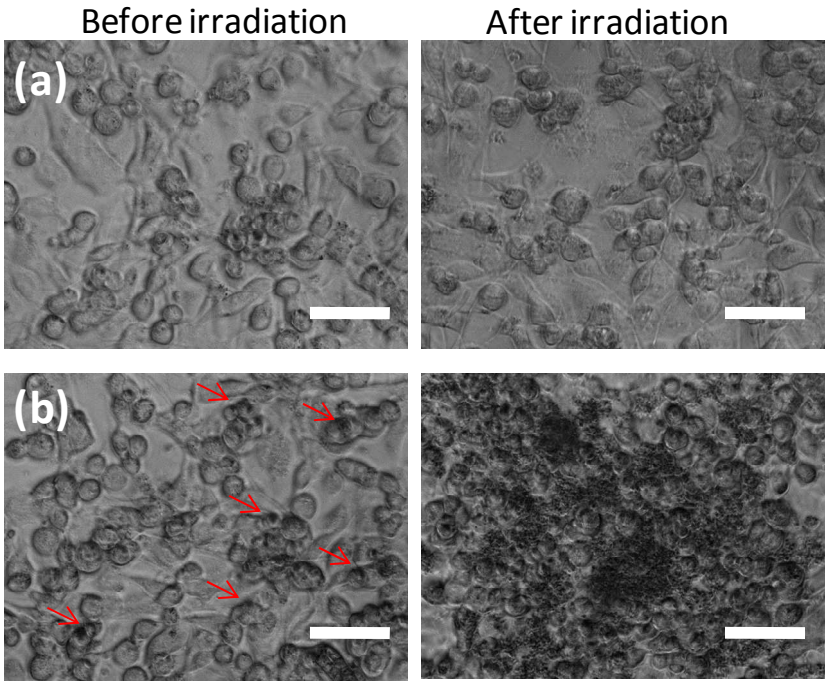

Figure S10. *In vitro* photodynamic activities of cGdots. Cellular morphology of MDA-MB231 breast cancer cells without (a) or with (b) pre-treatment of cGdots (500 μg/mL) for 2 h before and after laser irradiation for 30 min. Scale bar is 100 μm.

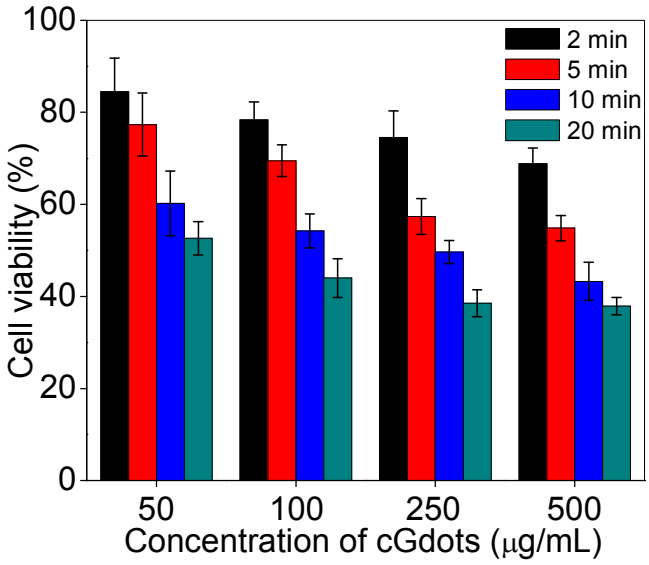

Figure S11. The viability of MDA-MB231 breast cancer cell with different concentrations of cGdots according to different exposure time of laser irradiation.

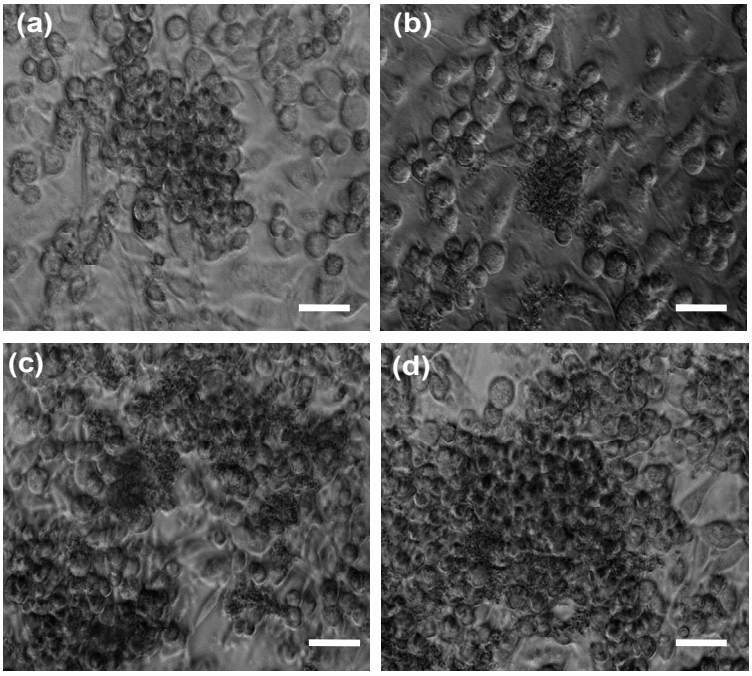

Figure S12. Time dependant cell viability was observed by optical microscope. Photo-sensitizing activities of cGdots changes of cell morphology after co cultured with cGdots and a) 2, b) 5, c) 10 and d) 20 min of laser irradiation. cGdots concentration was 500 μg/mL. Scale bar is 100 μm.

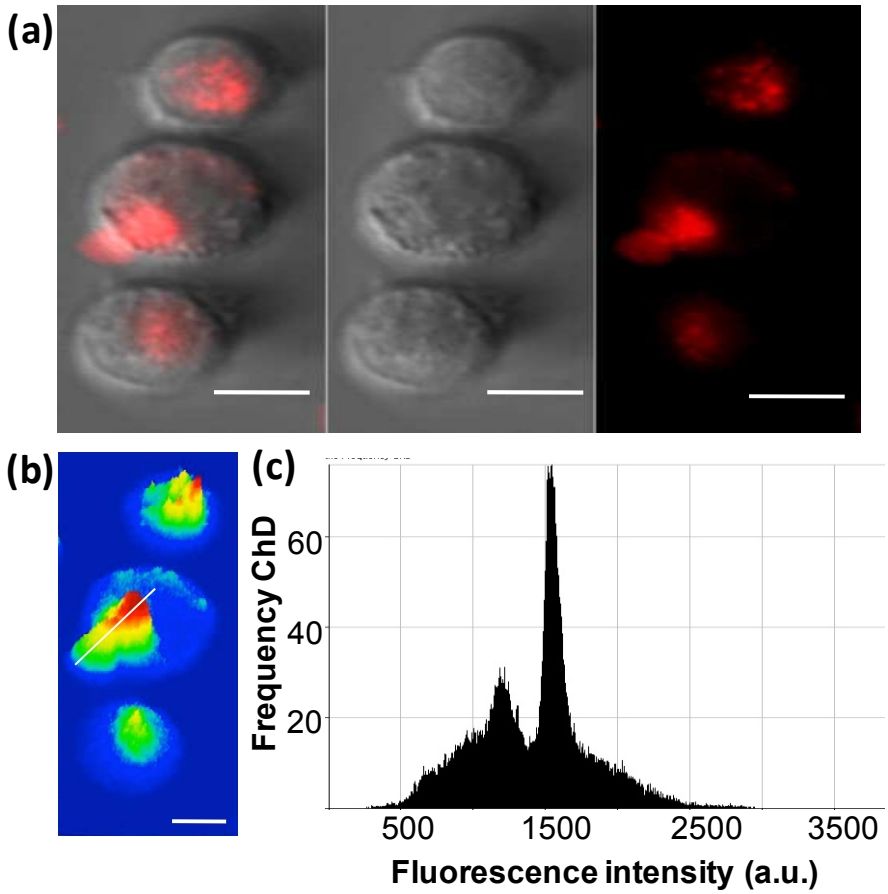

Figure S13. (a) Confocal laser scanning images of MDA-MB231 cells after treatment of cGdots (100 μg/mL). Scale bar: 20 μm. (b) 3-dimensional morphology of cGdots-treated MDA-MB231 cells with contour map. Scale bar: 20 μm. (c) Fluorescence intensities of cGdots-treated MDA-MB231 cell that was assigned with white line in (b).

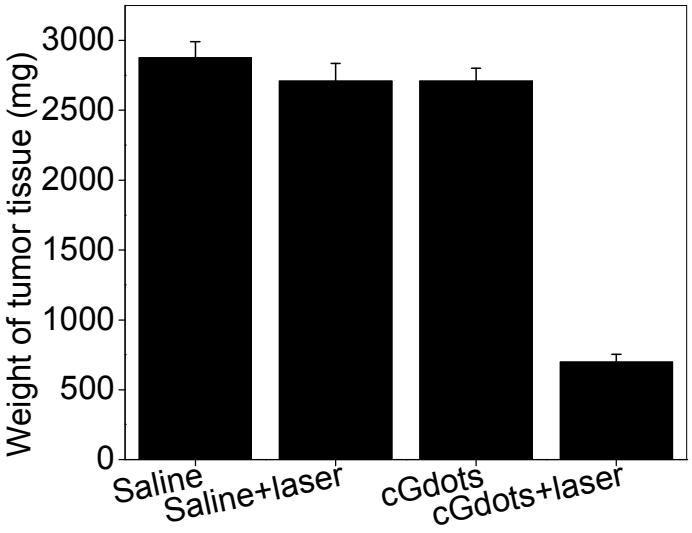

Figure S14. Weight of isolated tumor tissue of control and therapeutic groups. Data were plotted as mean±SEM (n=4).

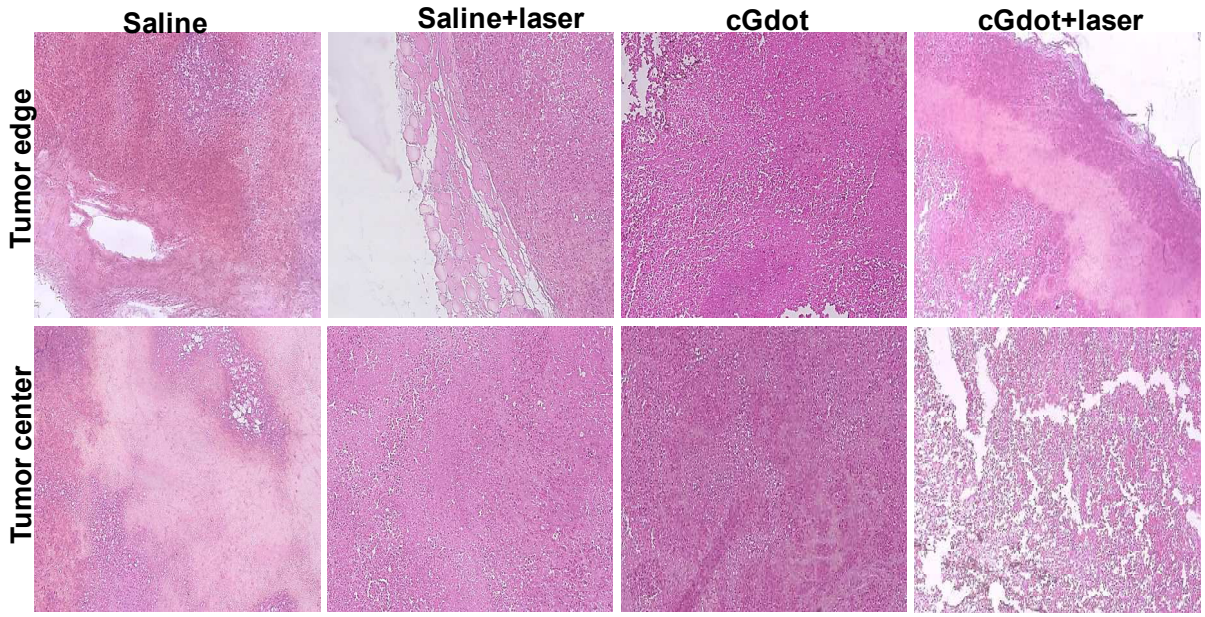

Figure S15. Histology images of tumor tissue. The tissue were collected from edge and center of tumor from saline, saline with laser, cGdots and cGdots with laser group mice. The histology data demonstrated maximum amount of cellular damage in the cGdots with laser treated tumor. The images also revealed that the thermal damage of the tissue collected from the center of tumor is higher than that of the tissue collected from the edges. It is because cGdots was intra-tumor injected through the center of tumor and photodynamic effect was effective over that portion of tumor (100X). The results also demonstrated that the cGdots itself is not toxic for tissue or cells as any damage observed in tissue of cGdots without laser group.

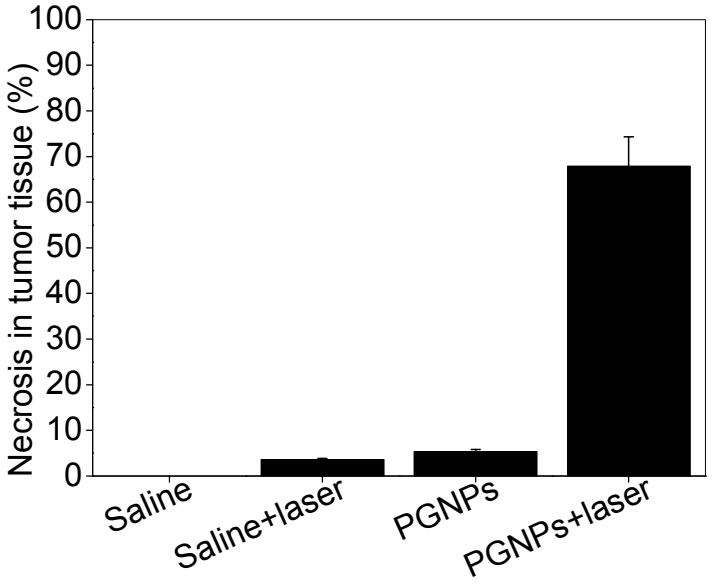

Figure S16. Tumors were isolated after 21 days of observation and weighed to observe the comparative weight variations among the different treated groups. The results revealed that the tumor growth of cGdots with laser group inhibited by around 70% compared to that of saline, saline with laser and only cGdots treated groups. Data were plotted as mean±SEM (n=4).

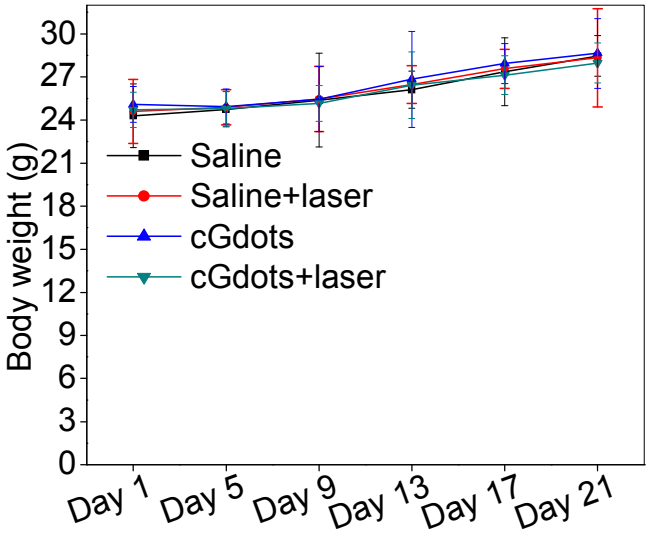

Figure S17. Body weights of saline, saline with laser, cGdots and cGdots with laser treated mice. The results showing no weight variation among the groups demonstrated no major toxicity occurred due to intratumoral administration of cGdots and laser irradiation. Data were plotted as mean±SEM (n=4).

References

[1] Li, L.; Nurunnabi, M.; Nafiujjaman, M.; Lee, Y.; Huh, K. M. GSH-Mediated Photoactivity of Pheophorbide A-Conjugated Heparin/Gold Nanoparticle for Photodynamic Therapy. *J. Control Release* **2013,** *171,* 241-250.

[2] Obaid, G.; Chambrier, I.; Cook, M. J.; Russell, D. A. Targeting the Oncofetal Thomsen-Friedenreich Disaccharide using Jacalin-PEG Phthalocyanine Gold Nanoparticles for Photodynamic Cancer Therapy. *Angew. Chem. Int. Ed.* **2012,** *51,* 6158-6162.