electron microscope. Their chemical composition such as the number of core atoms and number of protecting ligands is deduced using mass spectroscopic techniques.[33,34] Due to the very small size (~1 nm), they exhibit molecular transitions in absorption and emission and are totally different from the conventional metallic nanoparticles possessing surface plasmon resonance, and different synthetic approaches have been followed to make them. Because of the strong quantum size effect, quantum clusters possess characteristic absorption and emission profiles due to intraband and interband transitions[33,39] and can be distinguished from each other very easily from these features. Glutathione (GSH) protected gold quantum clusters[32−37] (Au_n-SG_m) (-SG, glutathione thiolate) is one such group of compounds which have been well known for some years. Glutathione is a tripeptide consisting of three amino acids, namely, glutamic acid, cysteine, and glycine. Out of the various glutathione-protected clusters such as $Au_{10}SG_{10}$, $Au_{15}SG_{13}$, $Au_{18}SG_{14}$, $Au_{22}SG_{16}$, $Au_{22}SG_{17}$, $Au_{25}SG_{18}$, $Au_{29}SG_{20}$, $Au_{33}SG_{22}$, and $Au_{39}SG_{24}$, $Au_{25}SG_{18}$ is the most thermodynamically stable one. The bigger clusters, $n > 25$, can be converted into $Au_{25}SG_{18}$ by adding excess glutathione. This extra stability of $Au_{25}SG_{18}$ arises due to the chemical inertness by the complete coverage of the gold core by glutathione ligands.[35] With the availability of these fluorescent molecular gold clusters, application of them in FRET becomes a distinct possibility. There has been no report to date using quantum clusters of gold in FRET. There have not been many applications of such quantum clusters till recently, particularly due to their unavailability in sufficiently large quantities. Various methods have been developed recently[34−38] to synthesize molecular clusters in gram quantities. Here we present the first report of the observation of FRET between the dansyl group (D) and the molecular cluster, Au_{25} (A), linked through glutathione. Efficient nonradiative transfer of energy from D to A occurs in femtosecond time scales.

2. Experimental Section

All chemicals were commercially available and used without further purification.

1. Synthesis of Glutathione-Capped Gold (Au@SG) Clusters. Glutathione-capped gold clusters were synthesized according to a reported method.[33] To 100 mL of 5 mM $HAuCl_4 \cdot 3H_2O$ in methanol, 20 mM reduced glutathione (GSH) was added. The mixture was then cooled to 0 °C in an ice bath for 30 min. An aqueous solution of $NaBH_4$ (25 mL, 0.2 M), cooled at 0 °C, was injected rapidly into this mixture under vigorous stirring. The mixture was allowed to react for another hour. The resulting precipitate was collected and washed repeatedly with methanol through centrifugal precipitation and dried to obtain Au@SG clusters as a dark brown powder. This product is a mixture of small nanoparticles and different clusters.

2. Synthesis of $Au_{25}SG_{18}$. $Au_{25}SG_{18}$ was synthesized from the as-prepared Au@SG clusters by ligand etching. The as-prepared Au@SG clusters were dissolved in 25 mL of water. GSH was added (20 mM) and stirred at 55 °C. The reaction was monitored by optical absorption spectroscopy. Heating was discontinued when the absorption features of $Au_{25}SG_{18}$ appeared in the UV−vis spectrum. This typically took 12 h of heating. The solution was centrifuged, and methanol was added to the supernatant to precipitate the cluster. The precipitate was dried to obtain $Au_{25}SG_{18}$ in the powder form. The prepared $Au_{25}SG_{18}$ shows characteristic UV−vis, FT-IR, and ^1H NMR features (Supporting Information 1).

3. Synthesis of Dansyl Glutathione (D-GSH).[40] A 140 mg amount of dansyl chloride (5-dimethylaminonaphthalene-1-sulfonyl chloride) in 2 mL of acetone was added dropwise to a solution of oxidized glutathione (150 mg) in aqueous NaOH (1.2 mL of a 1 M solution). The reaction mixture was allowed to stir for 30 min at room temperature. The mixture was then washed with diethyl ether twice, and the aqueous phase was lyophilized to give dansylated oxidized glutathione as a white powder. Nitrogen gas was bubbled into a solution of dansylated glutathione (285 mg) in 0.1 M Tris buffer (pH 8, 10 mL) for 10 min, after which dithiothreitol (DTT; 77 mg, 0.5 mmol) was added. The reaction mixture was stirred at room temperature for another 30 min under an atmosphere of N_2. The solution was adjusted to pH 4 with acetic acid and then lyophilized to give dansylated reduced glutathione. All experiments have been done with this reduced form. The synthesized dansyl glutathione is characterized by optical absorption and emission spectroscopy techniques and electrospray ionization (ESI-MS) (Supporting Information 2).

4. Functionalization of $Au_{25}SG_{18}$ with Dansyl Chromophore. Dansyl chromophore was attached to $Au_{25}SG_{18}$ by two routes.

(1) Direct Reaction of $Au_{25}SG_{18}$ with Dansyl Chloride. A 10 mg amount of $Au_{25}SG_{18}$ was dissolved in 5 mL of water. A 37 μL volume of NaOH was added, followed by 4.64 mg of dansyl chloride in 200 μL of acetone dropwise and stirred for 3 h. The product was precipitated by addition of methanol, centrifuged, washed three times with methanol and finally with ethanol, and dried to obtain a reddish brown powder.

(2) Exchange of Glutathione Ligands with Dansyl Glutathione. A 10 mg amount of $Au_{25}SG_{18}$ was stirred with 5.3 mg of synthesized dansylated reduced glutathione (D-GSH) for 3 h, and the product was precipitated by addition of methanol, centrifuged, washed three times with methanol and finally with ethanol, and dried to obtain a reddish brown powder.

Scheme 1 depicts the approaches used for functionalization of dansyl chromophore on Au_{25}. The products obtained after dansyl functionalization of $Au_{25}SG_{18}$ can be represented as $Au_{25}SG_{18-x}SGD_x$.

5. Details of Instrumentation. UV−vis spectra were measured with a Perkin-Elmer Lambda 25 instrument in the range of 200−1100 nm. Fourier transform infrared (FT-IR) spectra were measured with a Perkin-Elmer Spectrum One instrument. KBr crystals were used as the matrix for preparing the samples. High-resolution transmission electron microscopy of clusters was carried out with a JEOL 3010 instrument. The microscope was operated at 200 keV to reduce beam-induced damage of Au_{25} clusters. Nanoparticles were measured at 300 keV. The samples were drop casted on carbon-coated copper grids and allowed to dry in ambience. The Fourier transform nuclear magnetic resonance (FT-NMR) measurements were done with a JEOL 400 MHz instrument. The solvent used was D_2O. The electrospray ionization (ESI) mass spectrometric measurements were done with an MDX Sciex 3200 Q TRAP LC/MS/MS instrument in which the spray and extraction are orthogonal to each other. The samples taken in 1:1 water−methanol were electrosprayed at 5 kV. The spectra were averaged for 100 scans. Laser desorption ionization (LDI) mass spectrometric studies were conducted using a Voyager DE PRO Biospectrometry Workstation of Applied Biosystems MALDI-TOF MS. A pulsed nitrogen laser of 337 nm was used for the studies. Mass spectra were collected in positive-ion mode and averaged for 100 shots. Fluorescence measurements were carried out on a Cary Eclipse instrument. The band pass for excitation and emission was set as 5 nm. The experimentally obtained intensities in absorbance and emission as a function of wavelength, $I(W)$, have been