Supporting Information

H-Bonding Controls the Emission Properties of Functionalized Carbon Nano-dots

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(S1) Synthesis of nitrogen functionalized carbon nano-dots (N-CDs):

The water soluble nitrogen-functionalized carbon nano-dots (N-CDs) were synthesized by a microwave mediated hydrothermal process, wherein citric acid and urea were used as the carbon and the nitrogen source. Equimolar concentrations of citric acid and urea was prepared by dissolving 3 gm (1 mole) of citric acid and urea each, to 10 ml of de-ionized water (D.I. water) to form a transparent solution. The solution was then transferred to a borosilicate bowl and then subjected to a microwave radiation of power 700 W for about 5 minutes. This microwave treatment of the aqueous solution resulted in the formation of a brown aggregated cluster whose volume was observed to increase with time. The clustered mass was then crushed and dried in a vacuum oven at 80 °C for 1 hour. This process removes moisture and other volatile gases, like ammonia, which may have formed during the process of synthesis of the N-CDs. The brown powder was cooled down to room temperature and was then dispersed in water, forming a black murky dispersion. This liquid was then subjected to two successive steps of centrifugation (1500 G) and filtration (through a 10 kDa filter) to procure a pale yellow coloured aqueous solution of nitrogen functionalized carbon nano-dots (N-CDs). Tyndall effect was seen with a 5 mW laser pointer which elucidates the colloidal dispersion of the N-CDs in the water.

(S2) Dispersion of N-CDs in different solvents:

The aqueous solution of the N-CDs was freeze- dried at –80 °C and were lyophilized overnight to get a pale- yellow solid mass. The as-produced powder (0.25 mg) was taken and dispersed in 1 ml of different solvents. The solvents, used in this report, were carefully chosen which had their dipole moments and dielectric constants spread over a large spectrum. Table 1 lists the solvents used wherein they are arranged in their increasing order of di-electric constant. Thus, the dispersants were broadly categorized in three major classes which included the polar protic (water, ethanol and iso- propanol), polar aprotic (acetone, ethyl acetate, n- butyl acetate, dimethylformamide (DMF)) and non- polar solvents (1,4 dioxane and di- ethyl ether). However, in case of ethyl acetate and n- butyl acetate, the

N-CDs were transferred from water to the respective solvents. The upper phase of ethyl acetate was then collected for further studies. These dispersions of the N-CDs were stable in all the solvents, though no interaction was seen in highly non- polar solvents like hexane and pentane.

(S3) Characterization of N-CDs:

TEM images of N-CDs dispersed in water and ethyl acetate were obtained with Tecnai G^2 20 TEM, FEI, Netherlands, operating at 200 kV.

The crystallinity of the as-synthesized N-CDs was determined by a powder X-Ray Diffractometer (XRD). The aqueous sample of the N-CDs was lyophilized to obtained fine pale yellow powders. Characterization for crystallinity was performed using a Cu-Kα radiation at room temperature, with 2θ spanning from 0 to 80°.

Chemical characterization of the N-CDs, indicating the various functional groups present, was performed by Fourier transform infra- red spectroscopy (FTIR-Perkin Elmer) scanning over a wide window of wavenumbers from 500 to 4500 cm^{-1}. The lyophilized N-CDs were mixed thoroughly with a KBr pellet and analysed by FTIR.

The optical absorption spectra of N-CDs, dispersed in various solvents, were determined by UV-Visible- NIR Spectrometer (Jasco V- 530) at 298 K. Temperature dependent absorption spectra were obtained from a Jasco V-660 spectrophotometer where the temperature was varied from 298 K to 348 K. The N-CD dispersions were placed in a quartz cuvette with a path length of 1 cm. Concentration dependent absorption studies were obtained by dispersing varying amounts of N-CDs (by weight) in 1 ml of D.I. water.

Horiba Jobin Yvon Fluoromax-4 spectrofluorimeterwas used to study the steady state fluorescence of the N-CD dispersions, where the emission and the excitation slits were aligned at right angles to each

other. A covered four face cuvette, of path length 1 cm, was used for the measurements where both the excitation and the emission slit widths were maintained at 3 nm.

Lifetime decay of the N-CD dispersions were recorded by a Horiba Jobin Yvon Fluorocube instrument operating in the time- correlated single photon counting (TCSPC) mode. Excitation was induced by a 405 nm nano-LED operating with a pulse repetition rate of 1 MHz, and the decay was collected at different emission wavelengths ranging from 420 nm to 480 nm. Ludox AS40 colloidal silica (Sigma Aldrich) was used for collecting instrument response function (IRF). IBH software (DAS6) was used to fit the lifetime decay exponentially. A χ^2 value with $1.25 < \chi^2 < 1.36$ was assumed to be a good fit.

(S4) FTIR and XRD spectra for the as-prepared N-CDs:
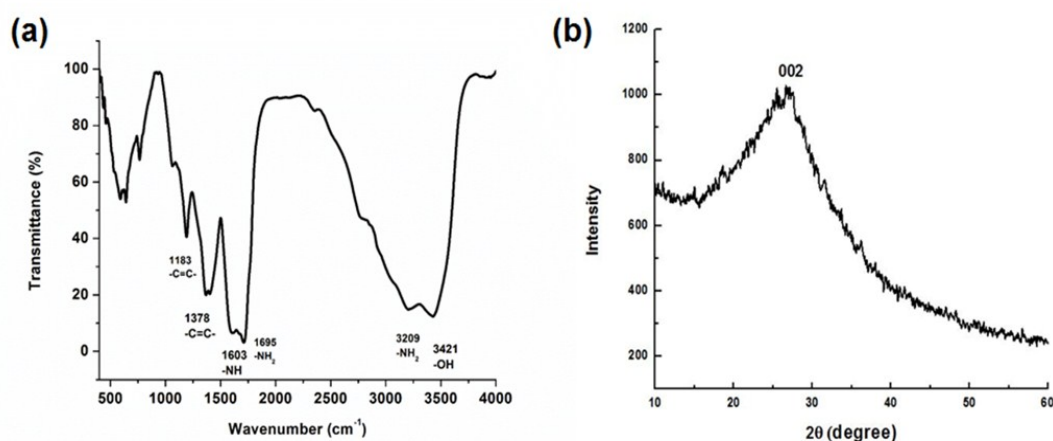

Figure S1. (a) FTIR spectra of the as-produced N-CDs. (b) XRD spectra of the N-CDs.

(S5) Mathematical model for the spectral shifts observed in the absorption spectra of nitrogen-functionalized carbon nano-dots dispersed in different solvents.

The presence of various hydrophilic functional groups (hydroxyl, carboxyl, carbonyl, ester and nitrogen containing amide and amine) on the surface and the edges of the nitrogen functionalized carbon nano-dots open avenues for the formation of hydrogen bonds between these nano-dots and polar solvents. However, such carbon nano-dots are not efficient hydrogen bond donors and hence limited interaction is observed with the N-CDs and the polar aprotic solvents and non-polar solvents. The expression is simple for non-polar and polar aprotic solvents due to their minimal interaction between the two species and is included in the report.

However for polar solvents, complex interactions arise which includes dipole-dipole and specific hydrogen bonding interactions. The former is a slow process and is not included while deriving the energy calculations. The changes in potential energy of the solvent-carbon dot diatomic molecule resulting from the charge transfer through hydrogen bonds are only taken in account. Thus, it is imperative to assume that the hydrodynamic diameter, consisting of the N-CD core and the surrounding molecules is not constant while deriving the mathematical expression for the energy states. The distance between the solvent molecules and the various functional groups present on the N-CD varies and is a function of the hydrogen bond donating capability of the solvent and the stabilization of either the ground or the excited state of these nano-dots. This has been illustrated by Figure S1, in the report, where each interaction of solvent molecule with the functional groups is assumed to be a di-atomic molecule (as illustrated by the dotted spheres in the same figure). Another assumption has been made while deriving the mathematical expression to understand the photo-physical properties of the N-CDs wherein, the energy required for exciting an electron from the ground state to the excited state was assumed to be equal to the net energy required to overcome the electric field due to the dipole formed by the electrons and the holes in the ground and the excited states respectively.
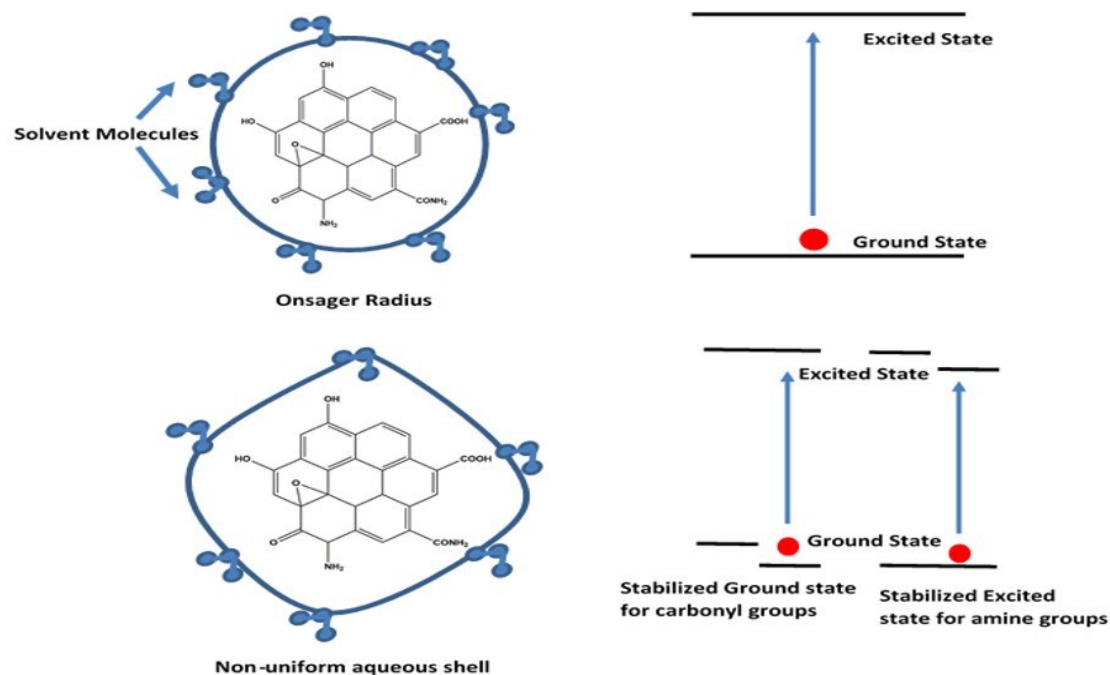
Figure S2. (a) No interaction takes place between the non-polar, polar aprotic solvent molecules and

(a)
the N-CDs. This results in the formation of a solvent shell around the fluorophore with an uniform

Onsager radius. (b) No change in bad gap of N-CDs occur due to the minimal interactions (c)When

dispersed in polar solvents, complex interactions take place resulting in a non-uniform aqueous shell

around the N-CD core. (d) Stabilization of ground state and excited states occur due to hydrogen

bond mediated charge transfers, resulting in either a blue or green shift in the absorption spectra.

Taking these considerations in account, the energy for each energy state (ground and the excited

states) is usually given by:

$$E = -\mu R_{electric} \tag{1}$$

where, R is the electric field and μ is the dipole moment of the carbon dot.

The electric field 'R' is an inverse function of the Onsager radius (radius of the imaginary sphere

containing the carbon dot core and the solvent molecules) which is again dependent on the Kamlet-

Taft's hydrogen bond donor capability of the dispersant. Taking the stabilization of different emission

states with various solvents in account, the net energy required to excite a N-CD was calculated by combining the energy differences associated with the nitrogen containing groups and the other hydrophilic (hydroxyl) groups. Applying the above equation, the excitation energy can be formulated as:

$$\Delta E = 2f(n)\left(\frac{\mu_E^2}{a^3} - \frac{\mu_G^{'2}}{a_G^{'3}}\right)_{carbonyl} + 2f(n)\left(\frac{\mu_E^{'2}}{a^{'3}} - \frac{\mu_G^2}{a_G^3}\right)_{amine} \tag{2}$$

Where, $\mu_G^{2'}, a_G^{3'}$ represent the stabilized ground state dipole moment of the fluorophore and radius of the solvent molecules around the carbonyl and carboxyl groups while $\mu_E^{2'}, a^{3'}$ stand for same terms in case of nitrogen-containing functional groups.

Rearrangement of equation 2 gives

$$\Delta E = \frac{2f(n)}{a^3}\left(\mu_{E(carbonyl)}^2 - \mu_{G(amine)}^2\right) + 2f(n)\left(\frac{\mu_E^{'2}}{a^{'3}amine} - \frac{\mu_G^{'2}}{a^{'3}carbonyl}\right) \tag{3}$$
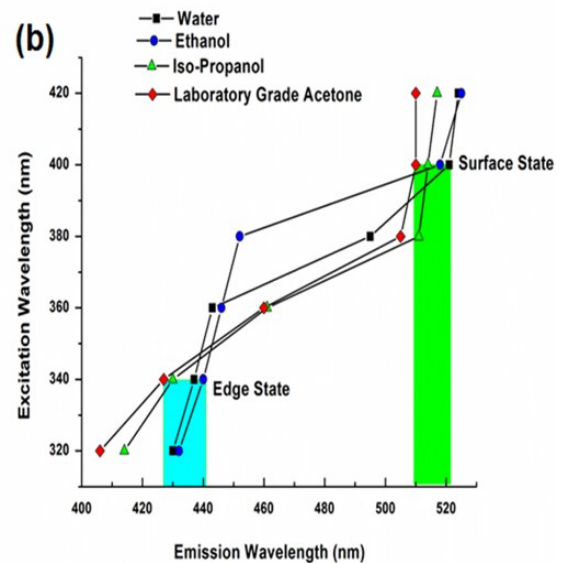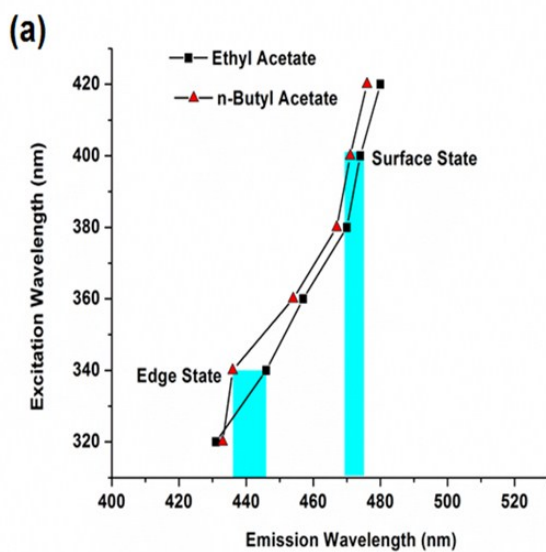
Figure S3. Role of surface states and edge states in the fluorescence from N-CDs dispersed in (a) different solvents and (b) polar aprotic solvents.
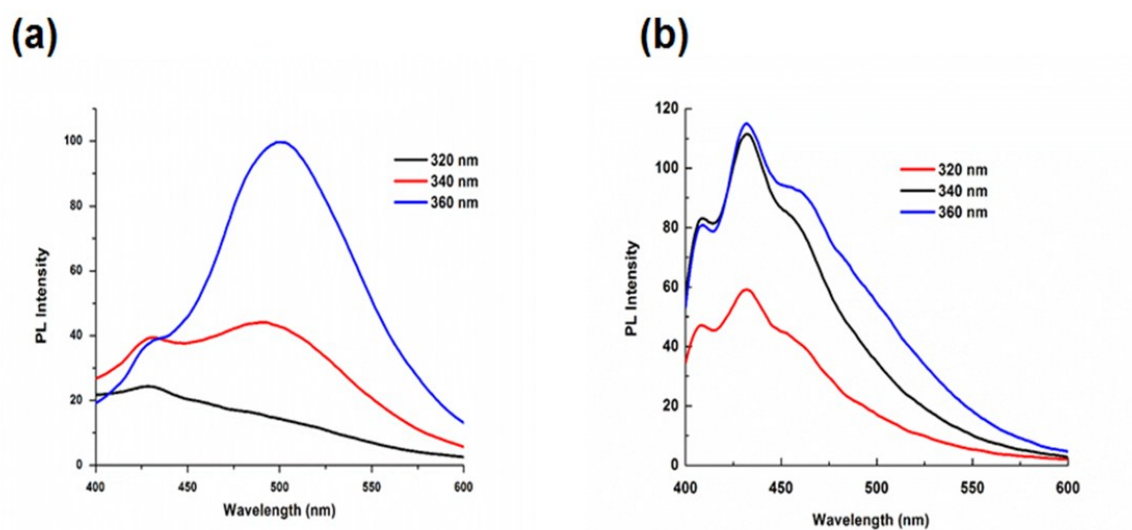

Figure S4. (a) Excitation dependent emission spectra obtained from N-CDs dispersed in laboratory grade acetone; (b) On removal of water from the hygroscopic acetone by sodium sulphate, an excitation independent emission was conceived from the carbon nano-dots.
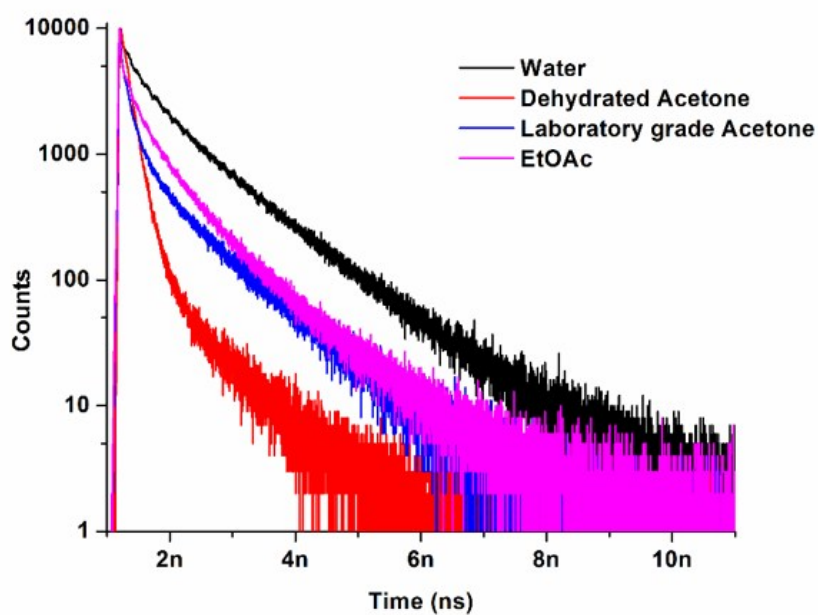
Figure S5. Comparative study of lifetime of N-CDs dispersed in different solvents

(S6) Calculation of the Quantum Yield (QY) of N-CD dispersed in different solvents:

The quantum yield (QY) of the N-CD were calculated against quinine sulphate in 0.1M H_2SO_4 as reference that has a quantum yield of 0.57 at an excitation wavelength of 350 nm. QY was calculated according to the following equation:

$$QY = Q_r X \left(\frac{I}{I_r}\right) X \left(\frac{OD_r}{OD}\right) X \left(\frac{\eta^2}{\eta_r^2}\right)$$

Where, QY and Q_r are the photoluminescence quantum yield of the sample and the standard (quinine sulphate). I and I_r are the integrated emission intensity of the sample and the standard. OD_r and OD are the absorbance of the standard and the sample respectively while η and η_r are the refractive index of the sample and reference solutions respectively

Fig. S6 shows the relation between the QY and the permittivity of the solvent used to disperse the N-CD, that can be fitted by an exponential function as:

$$QY = 15.344 \left(exp^{-\frac{\varepsilon}{46.59}}\right) -0.07$$

with R^2 being 0.874 while QY and ε being the quantum
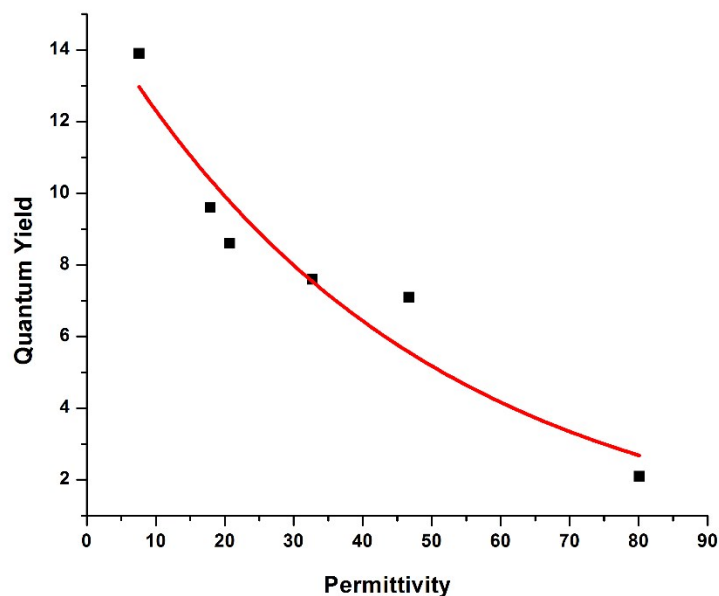
yield and permittivity of the solvent respectively.

Figure S6. Relationship between quantum yield and the permittivity of the dispersant.