Environment-dependent Emission Tuning in the Multicolor Nitrogen-doped Carbon Quantum Dots

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ABSTRACT: Carbon quantum dots (CQDs) are fascinating luminous materials from the carbonaceous family and are increasingly being investigated in many optoelectronic applications due to their unique photoluminescence (PL) characteristics. Herein, we report the synthesis of nitrogen-doped carbon quantum dots (NCQDs) from citric acid and *m*-phenylenediamine using a one-pot hydrothermal approach. The environment-dependent emission changes of NCQDs were extensively investigated in various solvents, in solid-state, and in physically assembled PMMA-PnBA-PMMA copolymer gels in 2-ethyl hexanol. The NCQDs display bright emission in various solvents as well as in solid-state and a temperature-dependent enhanced emission in gels. In detail, these NCQDs exhibit multicolor PL emission across the visible region and its enhancement upon changing the environment (solutions and polymer matrices). The NCQDs also exhibit excitation-dependent PL and solvatochromism, which are rarely observed in CQDs. Most CQDs are non-emissive in the aggregated or solid-state due to the aggregation-caused quenching (ACQ) effect, limiting their solid-state applications. However, these NCQDs display a strong solid-state emission centered at 568 nm ascribed to the presence of abundant surface functional groups, which helps to prevent the π - π interaction between the NCQDs and to overcome the ACQ effect in the solid-state. Interestingly, the NCQD containing gels display a significant fluorescence enhancement than the NCQDs in 2-ethyl hexanol solution because of the interaction between the polar PMMA blocks and NCQDs. This research opens up the development of large-scale, low-cost multicolor phosphor for the fabrication of optoelectronic devices, sensing, and bioimaging applications.

1. INTRODUCTION

Heavy metals-based semiconductor quantum dots (SCDs) such as CdSe, CdTe, and PbTe have been investigated as potential candidates for developing display and lighting applications owing to their unique characteristics such as high photoluminescence quantum yield (PLQY) and color tunability in the entire visible region.¹⁻⁴ However, these quantum dots are expensive for large-scale production and, because of the presence of heavy metals, are potentially toxic for humans and hazardous for the environment.

Carbon quantum dots (CQDs) are the most prominent alternatives to SCDs that do not have some of these limitations. CQDs have been increasingly popular in the last decade due to their unique optical properties and exciting characteristics such as ease of synthesis and subsequent surface modifications, low-cost, photocatalytic responses, and environmental friendliness.⁵⁻⁸ CQDs have already been investigated in various potential applications similar to the SCDs and additional applications such as medical diagnosis, drug delivery, sensing, solar cell, and photocatalysis.⁹⁻¹⁵ The aforementioned applications required fluorescence across the visible spectrum from blue to red with high PLQY. Hence, the tunable multicolor CQDs are highly desirable. CQDs have been synthesized through top-down and bottom-up approaches using various carbon precursors and small molecules, and most of these CQDs emit blue light.¹⁴⁻¹⁶ CQDs display strong luminescence and tunable photoluminescence (PL) characteristics, but despite recent progress, the underlying PL emission mechanism and excitation-dependent emission behavior still need further investigations.

Most of the CQDs reported in the literature are highly emissive in solution or in a dispersed state, but those are weakly emissive or non-emissive in the solid-state due to π - π stacking and

excessive resonance energy transfer between the fluorophores resulting in fluorescence quenching.^{17–19} This unwanted phenomenon, known as the aggregation caused quenching (ACQ) effect, generally occurs in most organic fluorophores.^{19,20} The ACQ effect could limit the applications of CQDs, especially in optoelectronic device fabrication, as the phosphor needs to be emissive in the solid-state. Therefore, achieving solid-state emissive CQDs is desired but challenging, and their emission mechanism is still debated.

Citric acid is a commonly available carbon precursor that has widely been used for the synthesis of carbon dots as the three carboxyl and one hydroxyl groups allow them to react with many small molecules and with themselves.^{21,22} Phenylenediamine isomers such as *ortho* (*o*-), *meta* (*m*-), and *para* (*p*-) phenylenediamines are also of significant importance for synthesizing polymers and many heterocyclic compounds.^{23–25} Phenylenediamine isomers as a nitrogen source precursor to prepare carbon dots using solvothermal method have been reported in the literature, but there are only a few reports on tunable multicolor emission characteristics obtained from this precursor.^{17,26–28} The full color (red, green, blue) tunable carbon dots were synthesized only from *o*-, *m*-, and *p*-phenylenediamines precursors through the solvothermal method and their applications in cellular imaging have been reported.¹⁷ Multicolor emission carbon dots synthesized from phenylenediamine isomers have been used as crosslinks to obtain alginate hydrogel.²⁶ In a recent study, multicolor emissive carbon dots have been synthesized using citric acid and *p*-phenylenediamine through hydrothermal process resulted in $\approx 29\%$ relative fluorescence quantum yield in 1-octanol.²⁸

Similar to various solvents, a polymeric environment can affect the emission properties of quantum dots. The enhanced emission observed in the graphene quantum dots (GQDs) - polymer blends [with regioregular poly(3-hexylthiophene-2,5-diyl) or poly(2-methoxy-5-(2-

ethylhexyloxy)-1,4-phenylenevinylene)] demonstrated significant improvement in the organic photovoltaic characteristics.²⁹ The fluorescence emission of maleimide functionalized GQDs has been restored (turn-ON) while interrupting the Froster resonance energy transfer system between tetrakis(4-aminophenyl)porphyrin and GQDs using glutathione molecule.³⁰

Herein, we report tunable multicolor nitrogen-doped carbon quantum dots (NCQDs) with strong solid-state luminescence, synthesized by the hydrothermal process using citric acid and *m*-phenylenediamine precursors. This is in contrast to the earlier reports on the fabrication of carbon dots from citric acid and *o*- or *p*-phenylenediamine as precursors, which have been reported to display lower absolute PLQY.^{28,31–33} The NCQDs synthesized here exhibit two interesting characteristics: (i) solvent-dependent emission property and (ii) excitation wavelength-dependent emission. The NCQDs display tunable photoluminescence nearly across the entire visible spectrum, and the solvent interaction with NCQDs has been investigated thoroughly. In addition to the multicolor emission in solution, these NCQDs display yellow emission in the aggregate or solid-state when excited with a 365 nm wavelength source. Further, CQDs have been embedded in a physical gel system, and the self-assembly process has been shown to uniquely enhance the emission intensity. Such solid-state emission behavior of carbon dots and incorporation in gel systems have rarely been reported in the literature.^{19,34,35}

2. EXPERIMENTAL

2.1. Materials. Citric acid, *m*-phenylenediamine (*m*-PD) with 99% purity, and 2-ethyl-1-hexanol (2EH) were used as received from Sigma-Aldrich. The following solvents were procured from Fisher Scientific company: chloroform, dichloromethane, acetone, acetonitrile, dimethylformamide, dimethyl sulfoxide, ethanol, methanol, iso-propanol and octanol. Deionized

(DI) water with the resistance of 18.2 M Ω .cm from Millipore Milli-Q purification system was used for all experiments.

2.2. Synthesis of NCQDs. Tunable and highly emissive NCQDs were synthesized by the hydrothermal reaction of citric acid and m-phenylenediamine. 20 mg of citric acid and 20 mg of m-phenylenediamine were dissolved in 10 ml of deionized water under stirring. The mixture was transferred into a 50 ml Teflon lined autoclave and then heated at 200 °C for 9 hours (Figure 1). The reaction temperature was slowly cooled to room temperature and then the brown color suspension was centrifuged for 5 minutes at 4000 rpm to remove fully carbonized particles. The supernatant solution was filtered through 0.2 μ m pore-sized PTFE membrane filter. The filtrate solution was concentrated by a rotary evaporator and then dried under a freeze dryer to obtain orangish-red colored NCQDs.

2.3. Gel Preparation. Acrylic triblock copolymer poly(methyl methacrylate)–poly(n-butyl acrylate)– poly(methyl methacrylate) [PMMA–PnBA–PMMA] (kindly provided by Kurray Co.) was used for the gel preparation in 2-ethyl-1-hexanol (2EH). Based on the manufacturer datasheet, the PMMA- and PnBA-block has a molecular weight of 9000 and 53000 g mol⁻¹, respectively.

For preparing the NCQD-PMMA and NCQD-PnBA solutions, respective homopolymers were purchased from Polymer Source Inc and were used as received. Based on the supplier datasheet, the PMMA has Mn of 7000 g/mol and Mw of 58400 g/mol with S:H:I tacticity of 35:55:10. The PnBA has Mn of 61,000 g/mol and Mw of 72,000 g/mol. Note that these polymers have molecular weight close to the blocks of the triblock copolymer. Considering the density of polymer (1.08 g/mL) and solvent 2EH (0.83 g/mL), the weight fraction can be converted to the volume fraction.

The pristine gel with 5% (v/v) was prepared by dissolving desired amount of polymer in 2EH and heated up to 80°C in a convective oven.^{36–38} After 5 hrs, a clear solution was obtained, which turned into a soft gel upon cooling to room temperature. To prepare the NCQD-Gel, using a polymer as basis 1% (w/w) of NCQDs were first dispersed into the 2EH using ultrasonication for 1800 s and then kept in an oven at 80 °C overnight to dissolve. This is referred to as an NCQDs-2EH solution. Once a clear solution was obtained, the desired amount of polymer was added to obtain 5% (v/v) NCQDs-Gel using the above procedure.

NCQDs-PMMA solution and NCQDs-PnBA solution were prepared by adding PMMA and PnBA homopolymers in the NCQDs-2EH solution. Here 1% (w/w) NCQDs concentration was maintained using the homopolymer weights as basis. The weight fraction of respective homopolymers was maintained as in the pristine gel. Both mixtures were heated for 5 hrs in a convective oven to obtain transparent solutions. Pristine homopolymer solutions (without NCQDs) were also prepared for reference.

2.4. Characterization. The morphology of synthesized NCQDs was investigated using TEM, JEOL 2100, operated at 200 kV. Few drops of a dilute NCQDs solution in ethanol were drop-casted on a copper grid for TEM imaging. The functional groups present in the NCQDs powder were characterized by Fourier Transformed Infrared spectroscopic (FT-IR) analysis (ATR mode) using a Nicolet 6700 FT-IR spectrometer (Thermo Scientific, USA). XPS analysis was performed using a Thermo Scientific K-Alpha XPS system equipped with a monochromatic X-ray source at 1486.6eV, corresponding to the Al K α line. A spot size of 400 μm^2 was used. Measurements were conducted in the Constant Analyzer Energy mode. The survey spectra were collected at pass energy of 200 eV over a range of 0–1300 eV. The high resolution (HR) core level spectra were collected at a 40 eV pass energy and an energy step size of 0.1 eV and using an average of 20

scans. HR scans of C1s, O1s, and N1s have also been conducted. XPS data processing was performed using “CasaXPS.” The dispersed particles on silicon wafers were characterized using AFM (Dimension Icon with ScanAsyst), primarily in the contact mode. Scanning was performed at a speed of 1 Hz, and a scan size of 50 μm was used. Gwyddion 2.38 SPM data visualization software was used to process the AFM images. Steady-state photoluminescence (PL) spectra were recorded on a Horiba Jobin Yvon Spectrofluorometer (FluoroMax-4). The solid-state fluorescence spectra were recorded using FS5 Edinburgh spectrofluorometer. The fluorescence lifetime experiment was carried out in different solvent polarities at 8 mM concentration by collecting the time-resolved fluorescence using the time-correlated single-photon counting (TCSPC) technique. A picosecond laser diode (LDH-P-C-405B; LDH series; PicoQuant) emitting photons of 405 nm was used to excite the NCQDs. The emitted photons were counted by a single-photon avalanche photodiode (SPAD), and the time-resolved data was collected using the TimeHarp 260 PICO interface with a resolution of 25 ps. UV-vis spectra were recorded with a UV-2450 spectrometer, in which each sample was placed in cuvettes (1.0 cm path length). The absolute PLQY were calculated using a 450 W xenon arc lamp (LH-450, M/s SLM Instruments), monochromator (Model no 77200, M/s ORIEL Instruments) to choose the excitation wavelength, integrating sphere (Model IS200-4, M/s Thorlabs) and a UV-Vis-NIR spectrometer (Flame 350-1000nm, M/s Ocean Optics) to record the scattered light/incident light and the fluorescence emission.

3. RESULTS AND DISCUSSION

3.1. Synthesis strategy & characterization. The schematic of the NCQDs synthesis is shown in Figure 1. Here, NCQDs were synthesized through a one-step bottom-up approach by condensation reaction and carbonization of citric acid with *m*-phenylenediamine precursors. As

shown in Figure 1a, the synthesis process involved mixing the equal mass of citric acid and *m*-phenylenediamine in water, followed by the hydrothermal treatment in a Teflon coated stainless steel autoclave at 200 °C for 9 hours (further details can be found in the experimental section). Here, citric acid and *m*-phenylenediamine are the primary carbon and nitrogen sources, respectively, in NCQDs. The synthesized NCQDs dispersed in water exhibited blue color under 365 nm (UV) illumination (Figure 1b). The structure of NCQDs consists of various functional groups.^{39,40} Especially, they have nitrogenous fused aromatic rings with sp^2 and sp^3 carbon domains (defined as core), and oxygenated species, viz., $-C=O$ and $-OH$. Also, the other

Figure 1. (a) The hydrothermal synthetic route for the preparation of multicolor NCQDs; b) The photographs of NCQDs dispersed in water in daylight (left), and under the illumination of 365nm (right), (c) Schematic illustration showing the hydrogen bonding of polar protic solvent molecules with surface functional groups of NCQDs.

functional groups, such as -C=O , -NH_2 , -O=C-NH_2 , -OH , and -COOH are present on the surface, particularly at the edges.⁴¹ The FTIR and XPS analysis can confirm the presence of these functional groups in the NCQDs.

The NCQDs were characterized by various techniques such as TEM, XRD, FTIR, and XPS analysis. The TEM image presented in Figure 2a indicates that the NCQDs are quasi-spherical, and we have not been able to capture any clear crystal lattice fringes (as explained at the end of this paragraph). The average particle size was found to be ~ 10 nm, and a representative NCQD with a diameter of ≈ 9.6 nm is shown in Figure 2a. The XRD pattern (Figure 2b) exhibits one broad peak at $\approx 19.32^\circ$ attributed to the highly disordered carbon (amorphous), corresponding to d -spacing of ≈ 0.46 nm, which is larger than the d -spacing (002 planes) of graphitic structure. The formation of an amorphous structure is likely due to the abundance of oxygen-containing surface groups (see below).³⁵

Figure 2. TEM images (a) a single NCQD at a higher magnification; (b) powder XRD pattern of NCQDs.

The surface functional groups of NCQDs were characterized by FTIR and XPS spectroscopic techniques. The FTIR spectra of NCQDs are shown in Figure 3a. The broad peaks appeared in the range of 3100-3542 cm^{-1} ascribed to the $-\text{OH}$ and $-\text{NH}$ stretching vibration, implying the presence of multiples of hydroxyl and amino groups present in the NCQDs. The aromatic $-\text{CH}$ stretching vibration peaks were observed in the range of 2919-2896 cm^{-1} . The strong absorption bands observed at 1700 and 1603 cm^{-1} are assigned to the $-\text{C}=\text{O}/-\text{COOH}$ groups from the edge of NCQDs and $-\text{C}=\text{N}-$ (formed from the condensation of carboxylic acid and primary amine) stretching frequency of NCQDs.

The surface functional groups and elemental composition of NCQDs were further characterized by XPS analysis. The XPS full scan spectrum, high-resolution XPS spectrum, and its deconvoluted spectra for carbon (C1s), nitrogen (N1s), and oxygen (O1s) of NCQDs are shown in Figure 3b-e. In Figure 3b, the full scan XPS spectrum exhibits three bands that appeared at 285.96 eV, 400.81 eV, and 532.96 eV. These correspond to the existence of carbon (C1s), nitrogen (N1s), and oxygen (O1s), respectively. The atomic ratio was found to be 69.64% (carbon), 7.58% (nitrogen), and 22.77% (oxygen), respectively. Further, as shown in Figure 3c, the C1s can be deconvoluted into four kinds of carbon species $\text{C}-\text{C}/\text{C}=\text{C}$ (sp^2C) at 284.68 eV, $\text{C}-\text{N}$ (sp^3C) 285.78 eV, $\text{C}-\text{O}$ at 287.88 eV, and $-\text{C}=\text{O}/-\text{C}=\text{N}$ at 289.08 eV. N1s spectrum can be fitted into three peaks at 399.18 eV, 400.18 eV, and 401.58 eV correspond to the pyridine N, amino N, and graphitic N, which confirm the successful incorporation of nitrogen in the carbon core structure during surface passivation (Figure 3d). Thus, N1s results indicate that the surface contains many nitrogenous fused aromatic rings (pyridinic N and graphitic N) in the core site and amino nitrogen and graphitic nitrogen at the edge site. Typically, the cores originate from the π -conjugated sp^2

Figure 3. Characterization of NCQDs. (a) FT-IR spectrum, (b) XPS full survey, and high-resolution XPS spectra for (c) C1s, (d) N1s, and (e) O1s

carbon domain in the carbon dots.⁴² Figure 3e, the O1s deconvoluted spectrum, shows that two

kinds of species C=O and C-O appeared at 531.88 eV and 533.48 eV, respectively.

We can identify the functional groups present on the surface based on the FTIR and XPS data, as XPS predominantly captures the surface functional groups. From these results, we illustrated the NCQDs structure (Figure 1c), which depicts the presence of nitrogenous fused aromatic structure rings with sp^2 and sp^3 domains in the NCQDs. Also, there are some defects that mainly arise from the amorphous carbogenic profile as exhibited by broad reflection in the XRD pattern. These defects consist of different oxygenic moieties such as C-O-C , -OH , and -COOH in the NCQDs. Therefore, FTIR and XPS results of NCQDs reveal that the synthesized NCQDs contain many hydrophilic groups such as -OH , -NH , -C=O/-COOH on the surface, confirming that the NCQDs were successfully passivated with nitrogen heteroatom. These surface functional groups make the NCQDs soluble in all common solvents, helping us study their photophysical properties in those solvents in detail.

3.2. Photophysical properties. The absorption spectrum of NCQDs suspended in deionized water was recorded and is shown in Figure 4a. The absorption spectrum exhibits a broad-band absorption with a strong peak at 220 nm in the range of 200-450 nm with a tail extended to the entire visible region, similar to that reported for nitrogen-doped CQDs prepared by other protocols.^{28,43,44} The absorption bands are mainly centered around ≈ 220 , 284, 380, and 492 nm.⁴⁵ The strong absorption bands from 210-295 nm correspond to the $\pi\text{-}\pi^*$ transition of -C=C- of sp^2 carbon core.^{46,47} The absorption shoulder from 348 nm to 492 nm is ascribed to the electronic transition of non-bonding orbital n (of -C=O/-C=N- and -NH_2 groups) to π^* orbital. The direct bandgap of NCQDs was determined from the Tauc plot shown in Figure 4b. The $(\alpha h\nu)^2$ versus E was plotted using UV-visible spectral data of NCQDs. Here, α is the normalized absorption

coefficient, $h\nu$ is the energy of the incident wave, and E is the photon energy. The energy bandgap (eV) calculated from the extrapolation of the linear region is 2.71 eV.^{39,48,49} The observed bandgap of NCQDs is consistent with the cyan color fluorescence emitted by exciting these particles with

Figure 4. (a) UV-visible spectrum of NCQDs in water and (b) the corresponding plot for $(\alpha h\nu)^2$ versus photon energy, E . The horizontal intercept of the tangent in (b) indicates the bandgap of NCQDs. (c) PL emission spectra of NCQDs for different excitation wavelengths. (d) The normalized PL emission spectra for different excitation wavelengths.

365 nm. The obtained bandgap value is slightly larger than the reported value (2.40 eV) of graphene quantum dots synthesized from coal materials.⁴⁹

The PL emission spectra of NCQDs in water excited at different wavelengths ranging from 300 nm to 450 nm at a 10 nm interval are shown in Figure 4c. With increasing excitation wavelength, the emission wavelength is red-shifted (bathochromic shift). This phenomenon is referred to as excitation-dependent PL emission.^{11,50,51} The excitation-dependent emission is observed more clearly in the normalized PL emission of NCQDs, as shown in Figure 4d. The normalized PL emission is obtained by dividing each emission intensity value by its maximum emission intensity. Here, for example, when excited at 300 nm, NCQDs emit blue light with the emission maxima centered at 431 nm, whereas exciting at 450 nm resulted in green color (502 nm). These results suggest that the emission of NCQDs can be made tunable from blue to green without changing any precursors, which has not been frequently reported for CQDs.^{52–54}

The synthesized NCQDs are well dispersed in the common polar aprotic solvents such as chloroform, dichloromethane, tetrahydrofuran, acetone, dimethylformamide, acetonitrile, and dimethyl sulfoxide, and polar protic solvents such as isopropanol, octanol, ethanol, methanol, and water. Also, these dispersions are very stable for a prolonged duration, as we have not seen significant changes in emission properties at least for two days. However, the NCQDs are not dispersible in non-polar solvents like hexane, toluene, etc. The broad dispersibility of the NCQDs enabled the detailed investigations of photophysical properties in various solvents. To characterize the interaction of NCQDs with solvents, we have recorded absorption spectra and steady-state PL spectra of NCQDs in different polar protic and aprotic solvents, as listed above. The absorption spectra of NCQDs in these solvents are displayed in Figure 5a and Figure S1. NCQDs in polar

aprotic and protic solvents display two to three absorption bands in the UV, and visible region 250-400 nm and 450-650 nm (except chloroform and dichloromethane). The absorption bands at higher energy region (200-300 nm) can be ascribed to the π - π^* transition of $-\text{C}=\text{C}-$. The absorption bands at 300-400, and 450-600 nm range correspond to the electron transition from n

Figure 5. (a) Absorption spectra of NCQDs in polar protic solvents; b) Normalized emission spectra of NCQDs in different solvents excited at 360 nm wavelength; (c) Emission maxima as a function of dielectric constants of solvents; (d) Lippert Mataga relationship capturing orientational polarization of hydrogen bonding solvents vs Stokes shift.

Figure 6. CIE diagram of NCQDs dispersion in (a) acetone, (b) tetrahydrofuran, (c) dimethylformamide, (d) methanol and (e) water with different excitation wavelengths.

orbital (induced by the weak electron donation groups as $-\text{OH}$, $-\text{NH}_2$ on the surface of NCQDs) to π^* orbital.^{49,55} The abundant N and O elements enhance the charge carrier density on the surface of NCQDs and induce the electron charge transfer towards the edge functional groups such as carboxyl, amino hydroxyl, and amide (the extended absorption band observed 450–650 nm shown in Figure 5a).²⁷

Different functional groups in the NCQDs can possibly interact with the solvent dipoles.⁴² This solvent-dependent phenomenon is called solvatochromism, usually attributed to intramolecular charge transfer. This behavior is commonly observed in organic fluorophore materials^{56,57} but has not been reported widely for the carbon dots. The excitation wavelength-dependent emission of NCQDs in water can be seen clearly in Figure 4c–d. We have recorded the PL emission spectra of NCQDs in different solvents by varying the excitation wavelengths

(Figures S2 and S3), and the corresponding CIE diagrams are shown in Figure 6. The CIE diagram depicts that the emission is red-shifted with the increase in the excitation wavelength. This is likely due to the presence of different emissive traps on the surface of NCQDs, which is responsible for the excitation-dependent emission property. Figure 6 displays that the emission color changes from blue to orangish-red in methanol and blue to green in other solvents when the excitation wavelength reaches 480 nm. These results confirm the highly tunable emission without changing any synthetic protocol and make them a promising material in optoelectronic applications.

To further understand the solvatochromism effect in NCQDs, we have recorded PL emission spectra in different solvents while excited at 360 nm. The normalized PL spectra are shown in Figure 5b. There is a red-shift of emission maximum with increasing solvent polarity. If the solvent polarity increases, the emission is shifted (red-shift) to the lower energy region due to the excited state stabilization by the polar solvent molecules. If the solvent polarity increases, the dipole moment of solvents affects the surface electronic state, resulting in a red-shifted emission wavelength.⁵⁸ The emission maxima is at 419 nm for THF, a less polar solvent, and that maxima shifts to 467 nm in a high polar solvent, such as water. The emission maximum in eV at different polar protic and aprotic solvents vs. the dielectric constant of the solvents are plotted in Figure 5c. The polarity parameters of different solvents and photophysical data of NCQDs in polar protic and aprotic solvents are tabulated in Table S1. The emission maxima are approximately linear to the dielectric constant of solvents, which confirms that both ground and excited states are sensitive to the solvent environment.

For more insight into the emission property with the solvent polarity, we have investigated the applicability of the Lippert-Mataga relationship. The orientational polarization that arises from the dipole moments of different polar aprotic and polar protic solvents was calculated from the

Lippert-Mataga equation.⁵⁹ The orientational polarizability versus Stokes shift values of different polar aprotic and protic solvents are plotted in Figure S4. The solvent-dependent emission property can be interpreted using the Lippert-Mataga plot, which displays a linear relationship between Stokes' shift and orientational polarization if the emission property depends on the solvent dipole moment. As displayed in Figure S4, the Stokes shift for NCQDs is not linear with respect to their orientational polarization if all solvents are considered. However, a linear relationship can be found for the alcohols considered here: octanol, isopropanol, ethanol, and methanol shown in Figure 5d. Thus, it can be inferred that the alcohols form hydrogen bonds (specific solvent interaction) with the functional groups present on the NCQDs surface.

The hydrogen bonding donation capability of solvents can be quantified by the well-known Kamlet-Taft parameter shown in Table S2. The polar protic solvents have a high α' (hydrogen bond donation) value than the polar aprotic solvents, and as a result, the $-OH$ group in the polar protic solvents form hydrogen bonds with the surface functional groups of NCQDs, as illustrated in Figure 1c. Also, the decrease in the emission intensity of polar protic solvents is due to the formation of specific solvent interaction that results in non-radiative decay. In the case of polar aprotic solvents, the NCQDs can donate the proton to the aprotic solvents (proton accepting capability) as conveyed moderately large β Kamlet-Taft value shown in Table S2. Thus, it can be concluded that the specific hydrogen bonding primarily dictates the photoluminescence characteristics of NCQDs in protic solvents, which leads to the excited state stabilization.^{60,61} In polar aprotic solvents, both strong hydrogen bonding acceptance basicity and dipole moment are responsible for the photoluminescence.

Figure 7. (a) Fluorescence lifetime decay and model fitting curve of NCQD in different solvents under ambient conditions (excitation at 360 nm; emission at 450nm). (b) Solid-state absorption and PL emission spectrum of NCQDs powder. (c) CIE diagram of NCQDs powder. (d) Fluorescence emission photographs of NCQDs powder under illumination of visible and UV 365 nm light.

To investigate further the solvent interaction with NCQDs, we have determined the absolute PLQY of the NCQDs in dimethylformamide, a polar aprotic solvent, and four alcohols such as ethanol, isopropanol, methanol, octanol, and water (polar protic). The Φ_F values vary between 14-30%, depending on the nature of the solvents (Table S3). The highest PLQY of ~30% was obtained in 1-octanol, whereas the lowest PLQY of ~14% in DMF. The NCQDs exhibit high

absolute PLQY in polar protic solvents and moderate value in DMF, a polar aprotic solvent. The PLQY of NCQDs in alcohols increases with an increase in the chain length (methanol → ethanol → isopropanol → octanol). The PLQY of NCQDs in alcohols majorly depends on the hydrogen bonding capacity, hydrophobicity & viscosity. Generally, if the chain length of alcohols increases, the hydrogen bonding ability decreases. In our case, the highest PLQY ~30% is obtained for octanol (long chain length alcohols), whereas the lowest value for methanol (short chain length). Therefore, the viscosity and the hydrophobicity of alcohols enable the restriction of intramolecular motion of the NCQDs, resulting in high PLQY. The same reason could be attributed to the decrease in PL intensity with an increase in polarity (discussed earlier in solvatochromism).

The PLQYs of NCQDs obtained in this work are higher than the earlier reported values for carbon dots in protic solvents obtained from the hydrothermal process, demonstrating that the PLQYs highly depend on the synthetic protocol.^{28,62,63} The high quantum yield and the CIE value of NCQDs (shown in Figure 6d) in the range of blue color (CIEy < 0.10) is highly desirable in deep blue light-emitting diode applications.⁶⁴ The fluorescence lifetime was measured in polar protic solvents such as deionized water, methanol, ethanol, isopropanol and, an aprotic solvent DMF and the results are shown in Figure 7a. The single exponential fit can capture the response reasonably well (Table S4) indicates that the observed fluorescence emanates from a well-defined electronic transition. As shown in Table S4, the average fluorescence lifetime of NCQDs in the solvents considered here firstly increased from 5.15 to 5.86 ns and then decreased to 5.6 ns with the polarity of the solvents. Therefore, our NCQDs exhibit the multicolor emission property with high PLQY by exciting them in different wavelengths and changing the solvent environment. This gives an easy way to switch from the existing environmentally hazardous quantum dots (CdSe, CdTe, and PbTe) to reduce the production cost and synthetic difficulties for multicolor

applications. With the unique emission properties in alcoholic solvents, our NCQDs could be a promising fluorescent probe for sensing compounds containing hydroxyl groups.

Interestingly, we have also observed the solid-state PL emission in the NCQDs powder, and this has been studied in detail. As shown in Figure 7b, the absorption spectrum of NCQDs powder shows three bands in the 200-300 nm range. These can be attributed to the π - π^* transition of the aromatic sp^2 carbon core. The band at 300-500 nm is due to n - π^* transition of hydrophilic functional groups $-C=N/-C=O$ and/or $-C-N$. Most of the CQDs or graphene quantum dots presented in the literature fluorescence strongly in the dispersed state or solution, but they emit weakly or display no emission in the solid-state due to the ACQ effect, which limits their applications in the solid-state.^{65,66} The PL emission spectrum of NCQDs powder indicates a strong yellow emission centered at 568 nm. We have calculated the CIE coordinates of NCQDs powder from the PL spectrum and found them to be (0.406, 0.475), further indicating that they emit yellow fluorescence (Figure 7c). There are abundant functional groups present in the surface of NCQDs preventing π - π interactions between multiple dots because of steric hindrance. As the π - π stacking and Forster resonance energy transfer process do not take place, the ACQ process is avoided, and the NCQDs emits in the solid-state.⁴⁵

In addition, the emission spectra of NCQDs powder were recorded by exciting the light from 300 nm to 600 nm wavelength. As shown in Figure S5, the 568 nm emission intensity first increases gradually with increasing the excitation wavelength from 300 to 500 nm at 20 nm intervals. The intensity of red-shifted emission maxima decreases when excited from 520 nm to 600 nm. This reveals that the solid-state NCQDs have a tunable emission property similar to that observed in water. Figure 7d displays the color of NCQDs powder captured under visible and UV

Figure 8. The photographs of (a) pristine acrylic gel, (b) NCQDs/gel (c) NCQDs/PnBA, and (d) NCQDs/PMMA samples under visible and UV 365 nm illumination. 365 light. The orangish-red under the visible light changes to bright yellow under UV light clearly capturing the redshift.

We have investigated the PL emission property of NCQDs by incorporating those in a physically assembled triblock copolymer acrylic gel, where the interactions between NCQDs, polymer blocks, and the solvent dictate the photophysical behavior. This gel, also known as acrylic gel, in the pristine form is prepared by dissolving 5% (v/v) ($\approx 6.41\%$ (w/w)) poly(methyl methacrylate)–poly(n-butyl acrylate)–poly(methyl methacrylate) [PMMA-PnBA-PMMA]

triblock copolymer in 2-ethyl-1-hexanol (2EH) at 80°C, followed by cooling the solution to room temperature (22°C).³⁶ The respective molecular weight of PMMA and PnBA in this polymer are 9000 and 53000 g/mol with 12.7% (w/w) of PMMA).^{67–69} At high temperatures, both PMMA- and PnBA-blocks are soluble in 2EH, resulting in a viscous polymer solution. With decreasing temperature, the solubility of PMMA becomes poor leading to the collapse of PMMA blocks, and the PMMA blocks physically associate in forming aggregates. These aggregates act as crosslinking points.³⁶ The PnBA solubility in 2EH does not change significantly with temperature, therefore, they remain soluble in solvent and bridge PMMA-aggregates. Consequently, a physically assembled three-dimensional polymer network is obtained.^{36–38,67}

To incorporate NCQDs in the gels, we prepared 1% (w/w) NCQDs-polymer samples by first dispersing the NCQDs in 2EH at room temperature (22°C) followed by the dissolving the PMMA-PnBA-PMMA (5% (w/w)) copolymer at 80 °C. These gels are referred to as NCQDs-Gel hereon. In addition, samples containing NCQDs and PMMA or PnBA homopolymers were also prepared in the same manner. The concentration (w/w) of PMMA and PnBA homopolymers in their respective solutions was the same as in the pristine gel, i.e., 0.81% and 5.60%, respectively. Further, NCQDs were added in both of these samples, maintaining the similar polymer to NCQDs ratio of 1% (w/w), as in the NCQDs-Gel. These samples are referred to as NCQDs-PnBA and NCQDs-PMMA here.

The NCQDs in 2EH exhibit blue color emission under UV 365 nm as shown in Figure 8a. The 5% (v/v) pristine acrylic gel does not display any fluorescence under UV 365 nm light (Figure

8b). Interestingly, NCQDs-Gel displays a bright blue color fluorescence, as presented in Figure 8c. Since NCQDs can interact with either or both block copolymer components, solutions of NCQDs and PMMA, and NCQDs and PnBA in 2EH were also exposed to UV light for further investigations. From Figures 8d and e, it can be inferred that the NCQDs dispersed PMMA solution displays a higher fluorescence than that dispersed in the PnBA solution. Figure 9a displays the PL

Figure 9. (a) The temperature dependent PL spectra of (a) NCQDs in 2-ethyl-1-hexanol, (b) NCQDs/acrylic gel, (c) NCQDs/PnBA, and (d) NCQDs/PMMA.

spectra of NCQDs in 2EH solution over a temperature range of 80 to 25 °C with a step of 5 °C. With decreasing temperature, no significant change in the luminescence intensity was observed. However, as displayed in Figure 9b, a significant increase in the intensity was observed for the NCQDs-Gel with decreasing temperature.

The change is significant at the higher temperature and appears to saturate as the temperature approaches room temperature. The PL intensity is approximately twice that observed in Figure 9a, for the same NCQDs concentration. Further comparisons were conducted by probing photoluminescence of NCQDs-PnBA and -PMMA solutions. As shown in Figure 9c, the PL intensity of the NCQDs-PnBA sample is weaker in comparison to the other samples and the temperature-dependent change is not significant. In contrast, the NCQDs-PMMA sample (Figure 9d) displays a higher PL intensity and that increases with decreasing temperature. This suggests that the PMMA facilitates the temperature-dependent photoluminescence intensity. Note that, in comparison to the NCQDs-Gel, the peak location is slightly shifted to the higher wavelength for the NCQDs-PMMA.

The carboxyl, hydroxyl and amino functional groups present on NCQDs surface can potentially interact with the oxygen group present in the PMMA via hydrogen bonds, leading to an enhanced luminescence.^{70,71} At lower temperatures, PMMA solubility in 2EH decreases and the NCQDs can act as nucleation sites for the collapsed PMMA chains. Because of enhanced interaction between NCQDs and PMMA, PL intensity increases. As shown in previous work, adding a few-layer of graphene (FLG) sheets in acrylic gels can slightly alter their gelation and mechanical properties.³⁶ Similar to the present case, FLG graphene sheets act as the nucleation sites for the aggregation of PMMA.

We have investigated the effects of NCQDs on the gelation and rheological properties of acrylic gels. Figure S6 displays the result of amplitude sweep experiments performed at room temperature. Here, storage and loss moduli (G' and G'') are plotted as a function of strain amplitude. Both of the gels display a similar response with similar G' and G'' values and stiffening behavior at higher strain amplitude. Figure S7 displays the G' and G'' as a function of temperature. Here the gelation temperature (T_{gel}) is considered as the crossover temperature of G' and G'' . For both gels, the gelation occurs at $\approx 33^\circ\text{C}$, and no significant change in T_{gel} with the addition of NCQDs was observed. We hypothesize that a small amount of NCQDs and smaller sizes in comparison to the FLGs have not caused any changes in the gelation and rheological properties. However, such a small amount resulted in the temperature-dependent photoluminescence properties of these gels. The self-assembled acrylic gels are widely studied as a model gel for understanding the mechanisms like cavitation and stiffening in biopolymers. The addition of photoluminescence functionality enables these gels to be utilized for temperature-dependent luminescence applications for thermal mapping and bioimaging. A future study will investigate such applications.

CONCLUSIONS

In this article, we reported yellow solid-state emissive NCQDs with multicolor tunability in the solution. These are synthesized via a simple one-pot hydrothermal process by using citric acid and m-phenylenediamine precursor. NCQDs exhibit excitation-dependent emission properties in the entire visible spectrum and solvatochromism effect. The emission color and PLQY of NCQDs can be tuned by altering the excitation wavelength and the surrounding environment. The red-shifted emission has been observed when NCQDs interact with both polar aprotic and polar protic

solvents. We studied solvent-dependent emission property changes using the Lippert-Mataga relationship. The results show that the emission maxima observed in different polar aprotic and polar protic solvents are approximately linear to the dielectric constant and orientational polarity of the solvents. In polar protic solvents, the NCQDs follow the regular trend in the emission shift depending on the specific hydrogen bonding between the surface functional groups present in the NCQDs with the solvents. The synthesized NCQDs emit blue color light in an aqueous solution and yellow color in a solid-state or powder form. Most earlier reports on the CQDs or CDs suffer from the ACQ effect in the solid-state or in aggregate, but our NCQDs overcome the ACQ and emit the yellow light in solid-state. These could be employed to fabricate solid-state light-emitting devices. Moreover, for the first time, NCQDs have been incorporated in a physically assembled triblock copolymer gel. These gels display unique temperature-dependent optical PL properties. The multicolor emissive NCQDs investigated here have potential applications in lighting devices, sensing, and bioimaging.

ASSOCIATED CONTENT

The detailed experimental procedure for absolute PLQY measurements, PL lifetime measurement, solvent polarity parameters and PL data of NCQDs in various polar aprotic and protic solvents, Kamlet-Taft parameters of different solvents, absolute quantum yield data, fluorescence lifetime data, absorption spectra NCQDs in polar aprotic solvents, PL spectra of NCQDs in alcoholic solvents and aprotic solvents with different excitation, Lippert-Mataga plot of NCQDs in various solvents, PL spectra of NCQDs powder, amplitude sweep and temperature sweep of pristine gel and NCQDs/gel.

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