Solvent Effect on Structural Elucidation of Photoluminescent Graphitic Carbon Nanodots

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ABSTRACT: Photoluminescence (PL) of carbon nanodots (CNDs) is proposed to originate from the polycyclic aromatic carbon-core and in situ synthesized molecular fluorophores. This work reports the CNDs prepared by direct pyrolysis of citric acid only at a prolonged time, 40 h, and their fluorescence emission parameters in a variety of solvents by steady-state and time-resolved emission spectroscopies. The response of fluorescence emission lifetime and emission quenching rate constants to changes in solvent parameters such as polarity and tumbling lifetime were essentially independent, unlike molecular fluorophores that display solvent-dependent emission parameters. Fluorescence emission was quenched in nitromethane additionally indicating to the polycyclic aromatic carbon-core as a predominant structural feature of the CNDs. The quenching of CND emission in the presence of benzophenone that has a strong triplet component in the excited state was observed. Quenching demonstrates the Stern−Volmer behavior and reveals the additional nonradiative decay pathways of CNDs. The main photophysical features of CNDs are discussed in terms of fluorescence emission originating from the excited state of the polycyclic aromatic carbon-core where contribution from the potential molecular fluorophores is considered minimal.

INTRODUCTION

Carbon nanodots (CNDs) are low-D carbon-based nanomaterials that attract much research effort due to their multifunctionality, biocompatibility, and environmental stability. Synthesis of CNDs is done by two methods: "top-down" and "bottom-up" approaches. The top-down approach is based on cutting larger higher-D carbon nanostructures such as graphene and carbon nanotubes into smaller nanoparticles, and the bottom-up approach is mainly based on pyrolysis or high-temperature treatment of molecular precursors into larger and more complex nanostructures. Recently, Ye et al. have also shown preparation of CNDs from coal as a low-cost carbon source with tunable photophysical parameters. The advantage of the bottom-up approach lies on the ease of the heteroatom doping step, which particularly results in enhancement of the bottom-up approach. Despite this advantage of the bottom-up approach, the nature of the PL emission along with the structure of the CND is not clear whether it is a single particle emitter, a molecular fluorophore, or a complex nanostructure with a covalently attached molecular fluorophore. An elegant study by Ehrat et al. showed that synthesis time can account the whole spectrum of transformation and formation of CNDs starting predominantly from molecular fluorophores at early stages of synthesis all the way to highly graphitized CNDs with dominant polycyclic aromatic structural features close to the end of the synthesis. On the other hand, a study on the effect of surrounding media, namely, solvent effect, revealed additional photophysical characteristics of the CNDs. Recent reports on the solvatochromic response of CNDs revealed important emission parameters.

This work reports the photophysical studies of CNDs prepared from citric acid only and in the prolonged synthesis quantum yields (QDs) reaching as high as 70%. Ambiguity on PL emission mechanisms arises from the fact the both polycyclic aromatic domains and 2-pyridone-based molecular fluorophores such as citrazinic acid reveal strong Stokes shifts. Therefore, the nature of the PL emission along with the structure of the CND is not clear whether it is a single particle emitter, a molecular fluorophore, or a complex nanostructure with a covalently attached molecular fluorophore.
time to address the emission properties of the undoped, well-defined, and highly graphitized CNDs.\textsuperscript{26} Luckily, CNDs prepared by this method were well soluble in a wide range of solvents. Solvent effects on PL emission were ascribed to a predominantly polycyclic aromatic carbon-core structure of the CND. The study also includes the photophysics of CNDs in nitromethane, which is known to be a fluorescence quencher of polycyclic aromatic hydrocarbons.

\section*{RESULTS AND DISCUSSION}

\textbf{Synthesis and Characterization of CNDs.} Various bottom-up synthetic methods for the CND preparation were reported, which include direct thermal pyrolysis, hydrothermal method, and microwave-irradiation-assisted procedure.\textsuperscript{27} Among many reported CNDs, the sodium salts of CNDs (Na$_2$CNDs) prepared by neutralizing with NaOH as reported by Reisner et al. exhibit successful application on photocatalytic reactions in an aqueous environment.\textsuperscript{26} CNDs treated with NaOH until pH = 7.0 resulted in water-soluble and sodium carboxylate terminated CNDs for further applications as stable photosensitizers in the photocatalytic hydrogen generation reaction. Microscopic analysis reveals that CNDs have an average particle size of 6.8 nm.\textsuperscript{26} In this work, synthesis of the CNDs was done according to the reported procedure by thermal treatment of citric acid at 180 °C for 40 h under air and used without neutralizing with NaOH. CNDs were also measured to have pH = 4.2. Due to the higher order of the polycyclic aromatic core structure that contributes to enhanced hydrophobicity, CNDs synthesized with this procedure were less soluble in water. A prolonged pyrolysis time and enhanced photostability of CNDs point to the robust and well-defined formation of the π-conjugated polycyclic aromatic core. This is also evident from the fact that these CNDs are less soluble in aqueous media and well soluble in various organic solvents. The comparison of TGA curves for both citric acid and CNDs confirms the formation of a more robust structure supported by a substantial increase in weight loss and thermal stability up to 280 °C for CNDs, versus 180 °C for citric acid (Figure S1). After 280 °C, CNDs gradually decompose to reach their most stable form at 800 °C with a total of 90% weight loss. In order to elucidate further on the chemical structure and surface functional groups of CNDs, additional characterizations were done. X-ray photoelectron spectroscopic (XPS) analysis of CNDs reveals surface O-bonding functionalities of the polycyclic aromatic π-conjugated carbon core (Table S1). The C/O ratio was found to be 2.6; upon irradiation for 20 s etching time, the ratio increased to 11.5, and subsequent etching for 40 and 60 s increased the C/O ratios to 17.5 and 20.6, respectively (Figures S2–S3 and Table S2). Prolonged etching resulted in an increase of the C/O ratio pointing to the loss of the oxygen functionalities and further carbonization upon etching under XPS conditions.

Figure 1a shows the survey scan, and Figure 1b shows the high-resolution XPS spectra (C 1s). From the deconvoluted C 1s peaks (Table S1), it is apparent that the oxygen-functionalized groups are predominantly (~22%) in the form of carboxyl or lactone (HO—C=O of O—C=O, 289.04 eV) groups. The deconvoluted O 1s peaks also reveal carbonyl (C=O, 531.94 eV) and C—O, 533.34 eV groups in 56 and 44% ratios, respectively (Figure 1c). It is noteworthy that the spectra were centered at 284.78 eV for the graphitic carbon (C—C/C=C). Relative contributions of each functional group are summarized in Table S1. XPS analysis reveals that CNDs are composed of a π-conjugated polycyclic aromatic core with carboxyl and carbonyl-functionalized groups at the edges. This conclusion is also supported by the Fourier transform infrared (FTIR) spectra shown in Figure 1d. The structural complexity of the CNDs resulted in broad and multiple absorption peaks at 2400–3690 cm$^{-1}$ that correspond to stretching vibrations of the O—H and C—H bonds. Similarly, the intense multiple peaks at 1625, 1712, and 1764 cm$^{-1}$ are related to the stretching vibrations of various C=O groups in the form of carboxyl, ester, or other forms of carbonyl. Additional insights on the chemical structure of the CNDs, particularly the quantitative analysis of the carbon structure and oxygen-functionalized groups, were done using

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\begin{figure}
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\caption{XPS survey spectrum (a) and high-resolution C 1s (b) and O 1s (c) spectra of the CNDs. FTIR spectrum (d) of CNDs shows various functional groups. Quantitative $^{13}$C NMR spectra (e); all C shown in blue and nonprotonated C and CH$_3$ shown in red.}
\end{figure}
13C solid-state nuclear magnetic resonance (NMR) spectroscopy. NMR data were analyzed based on the methodology developed previously by Johnson et al. Figure 1e shows the 13C NMR spectra of CNDs; in the quantitative spectra, all carbons are shown in blue and selected nonprotonated carbons are in red. Intense peaks resonated between 155 and 180 ppm correspond to carbonyl (C=O) corresponding to ester in the form of lactone and coumarin type groups and carboxylic acid (COOH) groups. Aromatic signals (graphitic) resulting from carbonization reaction are resonating at 100–150 ppm, and they comprise ~40% of all carbon peaks, including the fraction of both protonated in 60% of all aromatic carbons as shown in Figure 1e. It is also noted that the dominant signal observed at 35 ppm is from the methylene group (CH2) that is bridging the Figure 1e. It is also noted that the dominant signal observed at 35 ppm is from the methylene group (CH2) that is bridging the π-conjugated polycyclic aromatic core and carboxylic acid groups. The relatively flexible group (aromatic—CH2—COOH) features an important mechanistic detail as a noncarbonized functional group of precursor citric acid that contributes to the increased solubility of CNDs in a wide range of solvents. Based on the abovementioned methods of analysis and characterizations, it is concluded that the chemical structure of CNDs possesses a π-conjugated aromatic core with hydroxyl, carboxylic, dangling —CH2—COOH, and cyclic ester groups anchored on the edge as shown in Figure 2. The proposed structure of CNDs points to the close analogy of excited-state photophysical properties with coumarins.

Figure 2. Proposed model structure of CNDs prepared from direct heat treatment of citric acid under air.

**Steady-State and Time-Resolved Emission Spectroscopy.** CNDs synthesized using different methods show various solubilities in a wide range of solvents. Recently reported work describes the microwave-assisted synthesis of CNDs that were readily soluble mainly in polar and protic solvents. Steady-state and time-dependent fluorescence studies of the CNDs prepared in this work have been conducted in a broader range of solvents extending to less polar and nonpolar solvents such as acetone, tetrahydrofuran (THF), and dichloromethane (DCM). Here, the photophysical properties of CNDs in 10 different solvents were investigated (see Table 1 and Figure S4). UV–vis absorption spectra (see Figure S5) in all solvents show the broad absorption with a tail extending to 500 nm that is attributed to the higher energy π → π* transitions of the π-conjugated polycyclic aromatic carbon-core and lower energy n → π* transitions corresponding to surface carbonyl functional groups of CNDs. A distinct absorption peak of the n → π* transitions is often observed in heteroatom (such as nitrogen)-doped CNDs and shows a diminished intensity in undoped CNDs. Another view of such an absorption is also attributed to different charge-transfer states between individual CNDs. Figure 3a shows the normalized emission spectra of CNDs in various solvents with excitation at 365 nm. Emission maxima reported in Table 1 are in close range from 443 to 455 nm for all solvents.

**Figure 3.** (a) Steady-state photoluminescence emission spectra of CNDs in various solvents with excitation at 365 nm. (b) Representative fluorescence 3D-excitation-emission map of CNDs in acetone. (c) Excitation spectra and different excitation-dependent (inset: values of excitation wavelength) PL emission spectra of CNDs in acetone under ambient conditions. (d) Excitation spectra and different excitation-dependent (inset: values of excitation wavelength) PL emission spectra of CNDs in ethanol under ambient conditions.

**Table 1. Photophysical Data for CNDs in Various Solvents under Ambient Conditions**

| Solvent      | λ<sub>max</sub>, nm (365 nm λ<sub>b</sub>) | x | τ<sub>ave</sub> ns | τ<sub>1</sub> ns (%) | τ<sub>2</sub> ns (%) | τ<sub>3</sub> ns (%) | τ(295)<sub>b</sub> ps | k<sub>b</sub> M<sup>−1</sup> cm<sup>−1</sup> |
|--------------|------------------------------------------|---|-------------------|-------------------|-------------------|-------------------|-------------------|---------------------|
| acetic acid  | 451                                      | 1.06 | 3.9               | 1.1 (56)         | 3.2 (40)         | 10.5 (4)         | 9.06 × 10<sup>9</sup> |
| acetone      | 455                                      | 1.04 | 4.6               | 1.2 (54)         | 3.5 (42)         | 12.2 (4)         | 0.58              | 1.40 × 10<sup>10</sup> |
| acetonitrile | 454                                      | 0.99 | 4.6               | 1.4 (63)         | 4.0 (34)         | 12.9 (3)         | 0.26              | 1.11 × 10<sup>10</sup> |
| DCM          | 443                                      | 1.08 | 5.4               | 1.4 (59)         | 3.9 (35)         | 12.7 (6)         | 0.56              | 1.30 × 10<sup>10</sup> |
| DMF          | 449                                      | 1.12 | 3.3               | 1.0 (46)         | 2.7 (48)         | 7.7 (6)          | 0.91              | 1.81 × 10<sup>10</sup> |
| ethanol      | 453                                      | 1.00 | 3.2               | 1.0 (44)         | 2.5 (48)         | 6.5 (8)          | 16                | 1.65 × 10<sup>10</sup> |
| THF          | 451                                      | 1.05 | 4.4               | 1.3 (59)         | 3.7 (37)         | 11.6 (4)         | 0.94              | 1.76 × 10<sup>10</sup> |
| 1,4-dioxane  | 448                                      | 1.06 | 4.8               | 1.3 (49)         | 3.5 (45)         | 11.0 (6)         | 1.3               | 1.31 × 10<sup>10</sup> |
| water        | 450                                      | 1.04 | 3.6               | 1.2 (43)         | 3.1 (52)         | 8.5 (5)          | 0.41              | 1.75 × 10<sup>9</sup>  |
| nitromethane | 480                                      | 1.14 | 5.6               | 0.9 (46)         | 2.7 (44)         | 7.8 (10)         | 0.41              | 1.75 × 10<sup>9</sup>  |

<sup>a</sup>Average emission lifetime τ<sub>ave</sub> and emission lifetimes for three components τ<sub>1→3</sub>.<sup>b</sup>Lifetime of solvent tumbling from ref 44. Due to solubility of BzP, measurements on quenching were not conducted.
except in nitromethane that was red-shifted to 480 nm. Representative 3D-fluorescence plots of CNDs in acetone and ethanol reveal relatively broad and excitation dependent peaks (Figure 3b and Figure S6). PL-excitation spectra in both acetone and ethanol show distinct peak maxima at 370 nm, and PL-emission spectra show gradual excitation-dependent emission with changes in $\lambda_{\text{em}}$ maxima from 450 up to 600 nm in both acetone and ethanol (Figure 3c,d, respectively). The excitation peak at 370 nm indicates that the PL emission corresponds to mainly carbonyl excited-state moieties.\(^{26}\) Moreover, relatively moderate PL quantum yields (QY) of 2–3% were measured at $\lambda_{\text{ex}} = 370$ nm that have close correspondence with the previously reported analogous CNDs.\(^{26,30}\) Excitation-dependent emission of CNDs was often attributed to the multiple radiative emission states of CNDs, particularly from the carbon-core and carbonyl-functionalized edge groups.\(^{12,13,16}\) However, the exact contribution of the carbon-core and carbonyl-functionalized edge groups on PL emission is still not well understood. In addition, the effect of solvent on the excitation-dependent emission of CNDs studied in this work indicates that each local emissive state whether a carbon-core or carbonyl-functionalized edge groups does not affect the solvation dynamics. This is attributed to the much shorter lifetime of exciton redistribution between the carbon-core and edge functional groups. Therefore, for the clarity of the following discussion on PL emission of CNDs, both emission components, carbon-core and carbonyl-functionalized edge, will be designated as single emission from the polycyclic aromatic carbon-core.

Relatively low QY compared to nitrogen-doped CNDs and excitation-dependent emission of CNDs points to a more effective nonradiative emission mechanism in CNDs. On the other hand, molecular fluorophores exhibit excitation-independent emission.\(^{34}\) Changes in photophysical parameters of molecular fluorophores as a function of the solvent property are used as a powerful tool in deciphering the emission mechanisms.\(^{35}\) A full list of solvents used in this study is shown in Table 1. Stable dispersions in organic solvents and in water are formed (see Figure S4). PL emission decay spectra with $\lambda_{\text{ex}} = 365$ nm in various solvents were monitored (see Figure 4a) and fitted by a triexponential decay function (see Figure S7 for fittings). Triexponential fitting functions of decay profiles were also shown previously on analogous nanoparticles that were investigated by time-resolved emission spectroscopy.\(^{36}\) Table 1 summarizes the details of fitting parameters. Emission lifetimes are in the range of 3.2–5.6 ns. Relatively similar and solvent-independent appearances of the time profiles for three components are attributed to the different components within the same nanoparticle. Additionally, solvent-independent characters of all three components are consistent with their assignment as the faster diffusion of excitons of all three components within the lifetime of solvent vibration and tumbling.

Under a 365 nm excitation UV lamp, CNDs in various solvents show blue luminescence except in nitromethane. Previous studies have shown that nitromethane, on the other hand, is known to quench the fluorescence emission of alternant polycyclic aromatic hydrocarbons (PAHs) such as anthracene, pyrene, and larger PAHs and not quench the fluorescence emission of nonalternant PAHs such as fluoreanthene.\(^{37,38}\) Quenching of emission of CNDs in nitromethane, therefore,
points to the alternant nature of the emissive polycyclic aromatic structure of the CNDs (see Figure 2). Quenching of PL emission in nitromethane is caused by the excited core that generated diffusive excitons that result in ultrafast electron transfer to nitromethane. For the rest of the solvents, on the contrary, excitons diffuse to the edge of CNDs that result in recombination and edge-state emission. Similar values of lifetimes of components over the spectrum of solvents are attributed to the polycyclic aromatic carbon-core and edge structures of the CNDs that are free from molecular fluorophores, which often result in district solvent-dependent decay profiles.

To elucidate further the excited-state behavior of the CNDs, their excited-state quenching in the presence of benzophenone (BzP) was measured. BzP is known to quench PAHs through electron transfer (ET) as well as the triplet energy transfer (TT) quenching mechanism depending on the oxidation potential and triplet energy levels of the exited components.39 The redox potential of nitromethane is $−1.24 \text{ V vs SCE}$, and that of benzophenone is $−1.73 \text{ V vs SCE}$.40,41 Therefore, it implies that, in nitromethane, the quenching mechanism is predominantly through the ET process, where electron transfer is thermodynamically more favorable between excited CNDs and nitromethane that results in a decrease in fluorescence intensity. In the presence of BzP, which has a triplet energy of $E_T = 3.0 \text{ eV}$,42 the quenching mechanism could be competing between ET and TT processes. Quenching of excited CNDs was done in the presence of BzP in various solvents and is summarized in Table 1. Typically, quenching experiments were done with varying concentrations of BzP starting from 0.001 up to 0.4 M. PL of CNDs is nearly quenched at 0.4 M of BzP and shows linear dependence on quencher concentration.

Figure 5 also presents the Stern–Volmer plot, with $F_0/F$ versus [BzP]; analogous measurements in different solvents resulting in quenching rate constants ($k_q$) (see Table 1). Values of Stern–Volmer quenching rate constants exceed the kinetics of the diffusion controlled processes: $7.56 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ for all solvents except for nitromethane where $k_q = 1.75 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ and for acetic acid, $9.06 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$. This indicates that, except for nitromethane and acetic acid, in all other solvents quenching is static in nature, which indicates the strong coupling between CNDs and the BzP molecule in the excited state. In acetic acid, ground-state complexation between CNDs and BzP is prevented due to higher acidity. A slower quenching rate constant in nitromethane than the diffusion controlled rate constant points to the competing solvent participation in quenching processes in nitromethane as mentioned above. Using the relationship for the rate constant of fluorescence decay $k_q = \Phi_s \times \tau_{ave}^{-1}$ and by using the average lifetime (from Table 1) and quantum yields, the rate constant for radiative decay $k_s$ can be estimated to be $\sim 6 \times 10^6 \text{ s}^{-1}$. This is attributed to much faster nonradiative decay processes of excited-state CNDs. Fluorescence lifetimes of CNDs in the presence of BzP also reveal small changes as shown in Figure 4b and Table S3 pointing to the static nature of the quenching. Based on this, excited-state behavior of CNDs in the presence of quenching molecules nitromethane and BzP can be summarized as shown in Figure 6. PL emission quenching of CNDs in nitromethane can be attributed to singlet excited-state electron transfer, defined as charge separation rate $\tau_{cs}$ to more electron-deficient nitromethane. In the presence of BzP, in all solvents except for nitromethane and acetic acid, static quenching takes place, where an exciplex is formed between CNDs and BzP, $[^1\text{CND},^1\text{BzP}]$. Subsequently, $^1\text{BzP}$ that has lower reduction potential and efficient intersystem crossing rate, defined as $\tau_{isc}$, forms the BzP triplet state ($^3\text{BzP}$). Therefore, efficient triplet energy transfer rate defined as $\tau_{TT}$, can be another competing quenching process (see Figure 6).43 Further studies on shorter timescale exited-state dynamics of the CNDs have to be performed using ultrafast spectroscopic techniques to elaborate mechanistic details of the PL emission.

On the basis of the analysis of the PL emission parameters in various solvents, CNDs studied in this work have excited-state parameters that are essentially solvent-independent. This is in comparison to the other reported CNDs with solvent-dependent emission parameters, which indicate the existence of different types of emission centers such as a considerable fraction of molecular fluorophores in the structure.44 The strong resistance of emission parameters to solvent polarity parameter, $E_{f}(30)$, as shown in Figure S8, even in solvents with a large polarity difference such as water and dichloromethane, is also linked to the structural features of CNDs with the polycyclic aromatic carbon-core that has ultrafast redistribution of exciton population between three components. In fact, the straight line in the relationship between the quenching rate constant and lifetime of solvent tumbling $\tau(295)$ (see Figure 7), which was accurately measured for molecular dye coumarin 153,45 can be ascribed to the predominant carbon-core and molecular fluorophore free structures of CNDs reported in this work, and PL emission parameters reported in this work are mostly the components of the polycyclic aromatic carbon-core with edge-functionalized groups.

![Figure 6. Possible mechanisms of excited-state quenching for the CNDs/BzP pair in various solvents.](https://dx.doi.org/10.1021/acsomega.0c03375)
CNDs are known to have multiple emission components, and their two predominant mechanisms are contributions from the polycyclic aromatic carbon-core and molecular fluorophores. While molecular fluorophores often have solvent dependence on the PL emission parameters, CNDs reported in this work exhibit practically solvent-independent PL emission parameters. Further experiments on CNDs’ PL emission quenching in the presence of nitromethane and benzophenone reveal the static nature of emission quenching and provide additional evidence for the polycyclic aromatic carbon-core centered PL emission mechanism. Therefore, solvent independence points to the predominantly graphitic and polycyclic aromatic carbon-core structure of CNDs. Therefore, relatively lower QY for CNDs prepared by top-down methods can be attributed to the predominantly polycyclic graphitic structural feature, while higher QY for CNDs prepared by bottom-up methods can be due to multiple emissive centers including the presence of fractions of molecular fluorophores. Contribution of the molecular fluorophores to the emission mechanism of CNDs brings extra complexity and has a strong impact on further development of CNDs.

Photostability is an important property in development of efficient catalytic systems, while enhanced graphitization has been shown to increase the light absorption capacity and charge-transfer efficiencies of CNDs as photositzers. It is expected that this work can bring some important insight for understanding CNDs that is important for potential applications.

**EXPERIMENTAL SECTION**

**Materials.** Citric acid monohydrate, benzophenone, and all organic solvents were purchased from Millipore-Sigma and used without further purification. Ultrapure water was processed using a Milli-Q (Milford, MA, USA) system. CNDs were prepared according to the previously reported procedure. Briefly, citric acid was placed in a vial and heated under air at 180 °C for 40 h to produce a brown solid in 27% yield, which was used without further purification. Measurements in all solvents were done with concentrations of CNDs of 0.05 mg/mL solutions, except for water where due to lesser solubility, exact concentration was not measured.

**Characterization.** X-ray photoelectron spectroscopic (XPS) analyses were performed using a Thermo Scientific Escalab 250Xi spectrometer with Al Kα (1486.6 eV) as the X-ray source and operating resolution of 0.5 eV. X-rays with a 650 μm beam and pass energy of 100 eV were used for the survey scan, and 30 eV was used for the high-resolution scans. XPS depth profile measurement was performed by etching the analyte surface by an Ar-ion beam with 4 keV for 20, 40, and 60 s. XPS spectra was recorded after every etching cycle. High-resolution spectra for binding energies were centered at 284.8 eV corresponding to the C 1s of the graphitic carbon (C—C/ C=C). Fourier transform infrared spectra were obtained with a PerkinElmer 16F spectrometer using potassium bromide pellets. pH of CNDs in water under ambient conditions was measured using an Orion VersaStar Pro advanced electrochemistry meter from Thermo Scientific. Room-temperature optical absorption measurements were performed using a Genesys 10S UV–vis spectrophotometer from Thermo Scientific. An SDT Q600 TGA-DTA from TA Instruments was used to record thermal gravimetric analysis data (TGA). Typically, ~10 mg of sample heated up to 900 °C in aluminum pans at 10 °C min⁻¹ heating rate under N₂ flow. A Bruker 400 MHz spectrometer was used for solid-state ¹³C nuclear magnetic resonance spectroscopy at room temperature and operating at 125.65 MHz. The sample was packed into a 4 mm zirconia rotor, and cross-polarization magic angle spinning (CP-MAS) and high-power decoupling were used with a pulse delay of 5.0 s and a magic angle spinning rate of 10 kHz. Room-temperature steady-state photoluminescence (PL) spectra were recorded using a HORIBA Jobin Yvon Fluorolog-3 spectrofluorometer using a 450-W xenon lamp and excitation and emission slits of 1 mm with an integration time of 0.1 s. Time-dependent PL measurements were performed using a Hamamatsu Quantaurus-Tau fluorescence lifetime spectrometer. All of the spectra were recorded in ambient conditions using a 10 mm width quartz cuvette.

**ASSOCIATED CONTENT**

**Supporting Information**
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c02375.

TGA, XPS, UV–vis, fluorescence, decay and quenching profiles, photographs, and photophysical data for CNDs (PDF)

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