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# Stable Carbon Dots from Microwave-Heated Carbon Nanoparticles Generating Organic Radicals for In Situ Additions

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**Abstract:** Carbon dots (CDots) are small carbon nanoparticles with effective surface passivation by organic functionalization. In the reported work, the surface functionalization of preexisting small carbon nanoparticles with *N*-ethylcarbazole (NEC) was achieved by the NEC radical addition. Due to the major difference in microwave absorption between the carbon nanoparticles and organic species such as NEC, the nanoparticles could be selectively heated via microwave irradiation to enable the hydrogen abstraction in NEC to generate NEC radicals, followed by in situ additions of the radicals to the nanoparticles. The resulting NEC-CDots were characterized by microscopy and spectroscopy techniques including quantitative proton and $^{13}$C NMR methods. The optical spectroscopic properties of the dot sample were found to be largely the same as those of CDots from other organic functionalization schemes. The high structural stability of NEC-CDots benefiting from the radical addition functionalization is highlighted and discussed.

**Keywords:** carbon dots; radical additions; C-C linkages; stable structure/properties; nuclear magnetic resonance; characterization; optical spectroscopy



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## 1. Introduction

Carbon "quantum" dots, or more appropriately referred to as carbon dots due to the general lack of evidence for any classical quantum confinement effect, were originally found experimentally as preexisting and pre-processed small carbon nanoparticles with surface functionalization by organic species [1,2]. Such a structural configuration has since served as the basis for the classical definition of carbon dots, and as related, the dot samples derived from preexisting carbon nanoparticles have been designated in some literature reports as "classically defined carbon dots" (or commonly denoted as CDots, Figure 1) [1–3]. Despite the simple structure and ready synthesis of CDots, in the carbon dots research field most dot samples have been produced by "creating" the nanoscale carbon entities, which are presumed to be analogous to small carbon nanoparticles, via thermal carbonization of organic precursors [4–12].

Among the carbonization produced dot samples, the majority have been those obtained from simple thermal treatment of organic precursors in "one pot" under processing conditions that are generally much too mild (such as thermal processing at less than 200 °C for a few hours) for any meaningful, let alone sufficient, carbonization. Consequently, such samples generally contain only a rather small or negligible amount of non-molecular nano-carbons, which not only defeats the essence of carbon dots but also enables serious contamination in the samples by colored molecules and/or molecular

chromophores [13–15]. In some cases, the molecular dyes and/or chromophores, which are products from chemical reactions of the organic precursors made possible by the thermal processing conditions that are insufficient for the intended carbonization but enough in thermal energy for chemical processes, could dominate the observed optical spectroscopic properties of the samples to lead to wrong conclusions and/or erroneous claims [16–20]. As increasingly recognized in recently reported studies [16,19,21–24], the synthesis of dot samples containing a significant amount of non-molecular nano-carbons, again the essence of "carbon dots", requires more vigorous thermal processing conditions such as higher processing temperatures coupled with longer treatment times for more meaningful carbonization of the organic precursors. The dot samples thus prepared are composed of nano-carbon entities or domains (similar to tiny carbon nanoparticles) embedded or dispersed in abundant organic species (mostly the crosslinked organic precursors, with the nano-carbons for the crosslinking, for example). Therefore, these appropriately carbonization produced dot samples with their composite-like structure and morphology are different from classically defined CDots (Figure 1), and they may be considered as "nano-carbon/organic hybrids" (the "hybrids") [24]. However, since both the "hybrids" and CDots contain structural elements of nano-carbons passivated by organic species, thus agreeing with the definition of carbon dots, they share some of the characteristic optical spectroscopic and related properties, as observed experimentally [22,25].

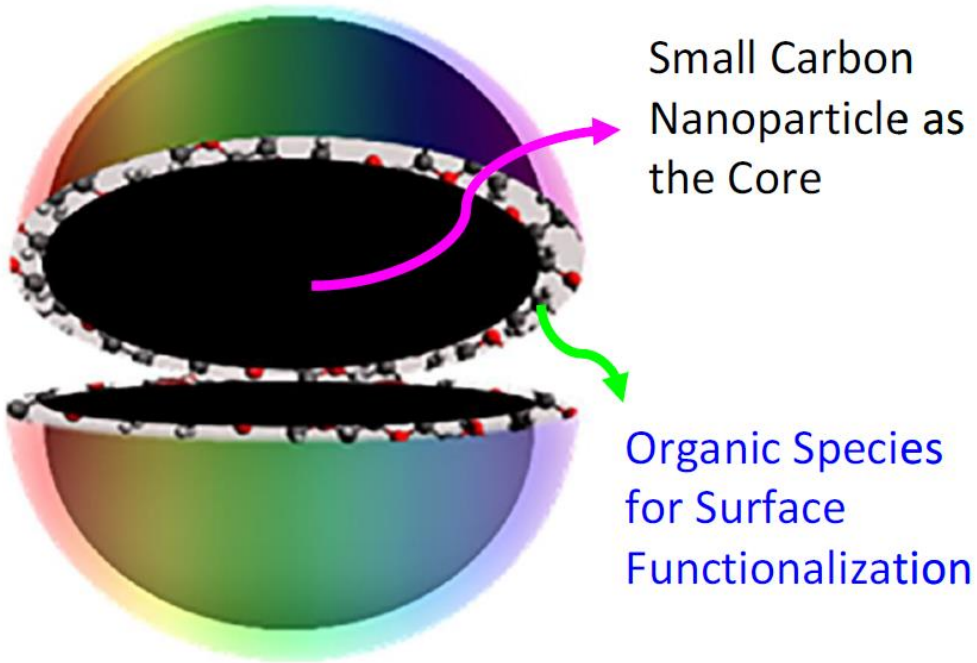


**Figure 1.** Cartoon illustration on the classically defined CDots obtained from the deliberate chemical functionalization of pre-existing small carbon nanoparticles.

Microwave irradiation has been used as a convenient and efficient energy source for the thermal carbonization of organic precursors, and also in the synthesis of CDots. As in the original finding [1,2], CDots have often been prepared by amidation chemistry to couple amino molecules with the carboxylic acid moieties on the surface of preexisting small carbon nanoparticles that are typically induced in the oxidative acid treatment to harvest the nanoparticles from carbon nanopowder samples [26–28]. While amide linkages are generally considered robust in nature, the carbon nanoparticle surface may only be able to accommodate a limited number of carboxylic acid groups, subject also to other limitations such as the vulnerability to decarboxylation, which could negatively impact the effectiveness in the carbon nanoparticle surface passivation by the organic functionalization and the structural stability of the resulting CDots. On the other hand, there is

significant experimental evidence suggesting that small carbon nanoparticles can accommodate radical additions, for which a representative example has been the efficient radical copolymerization of small carbon nanoparticles with vinyl molecules [29,30]. By extension, oligomers or small molecules capable of forming organic radicals under specific reaction conditions may also be used for the functionalization of small carbon nanoparticles via radical additions to yield structurally stable CDots. One example among small molecules is *N*-ethylcarbazole (NEC, Figure 2), in which the α-hydrogens are vulnerable to abstraction under special reaction conditions created by microwave irradiation to form NEC radicals, followed by their in situ additions to the small carbon nanoparticles to obtain structurally stable NEC-CDots (Figure 2) [31]. Of particular interest in such a reaction and the outcome is the unique role of the small carbon nanoparticles, which could apparently make it possible to differentiate the microwave irradiation for radical generation and in situ additions from the similar microwave processing for the above discussed largely random carbonization of organic species. In the work reported here, the microwave processing as an effective synthetic approach for CDots of high structural stability was investigated in more detail, with a more quantitative account for the preferential microwave heating of carbon nanoparticles in the presence of organic molecules such as NEC enabled by their very different microwave absorption abilities. The nanoparticle-centric synthetic process driven by the preferential microwave absorption may be used as a mechanistic justification for the observed similarity between NEC-CDots and other CDots obtained from amidation chemistry. The improved characterization results of the dot sample and correlations between the structural stability and observed stable photophysical properties and parameters demonstrate the advantageous characteristics of the microwave-assisted radical additions for CDots of stable structure and performance. The general applicability of the synthetic approach is discussed.

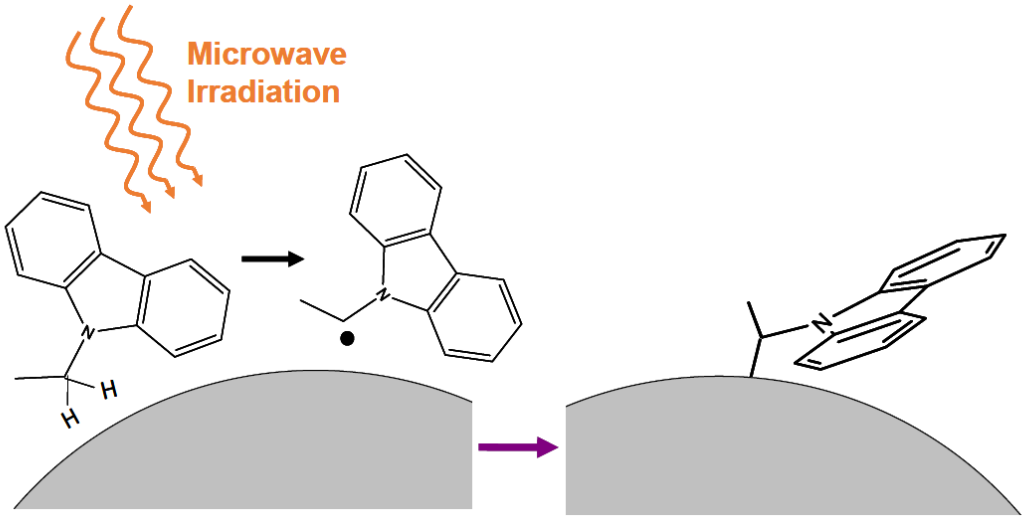


**Figure 2.** The reaction scheme on the selectively and rapidly heated small carbon nanoparticle enabling the hydrogen abstraction to generate NEC radical on the nanoparticle surface for the in situ addition.

## 2. Experimental Section

### *2.1. Materials*

The carbon nanopowder sample containing small carbon nanoparticles of less than 20 nm and largely amorphous was purchased from US Research Nanomaterials (Houston, Texas), and *N*-ethylcarbazole (NEC, 99.9%) from Beantown Chemical. Nitric acid (69.3%, water for the rest), toluene (99.9%), and hexanes (ACS grade) were supplied by Fisher Scientific, THF (>99%) by Alfa Aesar, and chlorobenzene (>99%) by Acros. Deuterated solvents for NMR measurements were obtained from Cambridge Isotope Laboratories.

### 2.2. Measurement

UV/vis absorption spectra were recorded on a Shimadzu UV-3600 spectrophotometer. Fluorescence spectra were measured on a Jobin-Yvon emission spectrometer equipped with a 450 W xenon source, Gemini-180 excitation and Triax-550 emission monochromators, and a photon counting detector (Hamamatsu R928P PMT at 950 V). NMR measurements were performed on a Bruker Advance 500 NMR spectrometer. Atomic force microscopy (AFM) images were acquired using a Nanosurf CoreAFM instrument and a Molecular Imaging PicoPlus AFM system in the acoustic AC mode. Transmission electron microscopy (TEM) images were obtained on a Hitachi H-9500 high-resolution TEM system.

### 2.3. NEC-CDots

The processing of the carbon nanopowder sample for the harvesting of small carbon nanoparticles, and their subsequent use in the microwave-assisted functionalization reaction for NEC-CDots were following the previously reported protocols with some modifications (see Supplementary Materials).

## 3. Results and Discussion

NEC is not an active molecule, though the α-hydrogens (Figure 2) are more susceptible to abstraction under more extreme reaction conditions. As related, even with the abstraction the resulting NEC radical is expected to be very unstable and short-lived. Therefore, in order to facilitate the hydrogen abstraction to be followed immediately by the radical addition to small carbon nanoparticles, namely the radical addition in situ, what is required is for the carbon nanoparticles to participate in the hydrogen abstraction to produce organic radicals for in situ additions to themselves. Such a requirement can be achieved via microwave heating of small carbon nanoparticles in the presence of NEC molecules, in which the absorption of microwave energy by the nanoparticles results in ultra-hot particle surfaces to enable the hydrogen abstraction for NEC radicals. The microwave-assisted processing takes advantage of the much higher microwave cross-section (the "dissipation factor") [32] of carbon nanoparticles than those of typical organic molecules such as NEC [33,34]. More specifically at the operational microwave frequency of 2.45 GHz commonly used in commercial microwave ovens, the available experimental results show that the dissipation factor of carbon nanoparticles is nearly an order of magnitude larger than that of NEC related organic species [32,34]. In the experiment for the dot synthesis, small carbon nanoparticles were mixed well with NEC for the desired configuration of individual nanoparticles each surround by NEC molecules in the final solid-state mixture. The mixture was heated in a conventional microwave oven to yield adducts of the small carbon nanoparticles surface functionalized with NEC species, thus classically defined NEC-CDots (Figure 2). Because of the sharp contrast in the microwave dissipation factors, the small carbon nanoparticles are heated very efficiently, but the NEC fraction in the mixture is relatively transparent to the microwave irradiation with only minor carbonization under the processing conditions, as also confirmed in the separate control experiment with neat NEC only without any carbon nanoparticles. The as-prepared dot sample was cleaned in conventional organic chemistry procedures, including repeated anti-solvent precipitations to remove molecular NEC and/or derivatives and their minorly carbonized species.

NEC-CDots are soluble in polar organic solvents, similar to CDots of other surface organic functionalities. As compared in Figure 3, the optical absorption and fluorescence emission properties of NEC-CDots are largely the same as those of EDA-CDots prepared by the amidation chemistry with the small diamine 2,2′-(ethylenedioxy)bis(ethylamine) (EDA) for dot surface functionalization [27]. The featureless absorption spectra (Figure 3) are little changed from that of the suspended small carbon nanoparticles [27], suggesting that the functionalization does not meaningfully change the electronic transitions in the small carbon nanoparticles. Additionally, shared between the two dot samples synthesized in different approaches, radical addition for NEC-CDots versus amidation chemistry for EDA-CDots, are their fluorescence spectral features and especially the characteristic excita-

tion wavelength dependencies. Since the dramatic enhancement of fluorescence brightness associated with the carbon nanoparticle surface functionalization is mechanistically attributed to the effective passivation of surface defects by the organic functionalization [1–3], the observed similar fluorescence emission properties (Figure 3) support the notion that the functionalization via radical additions is just as effective for the desired passivation of surface defects.

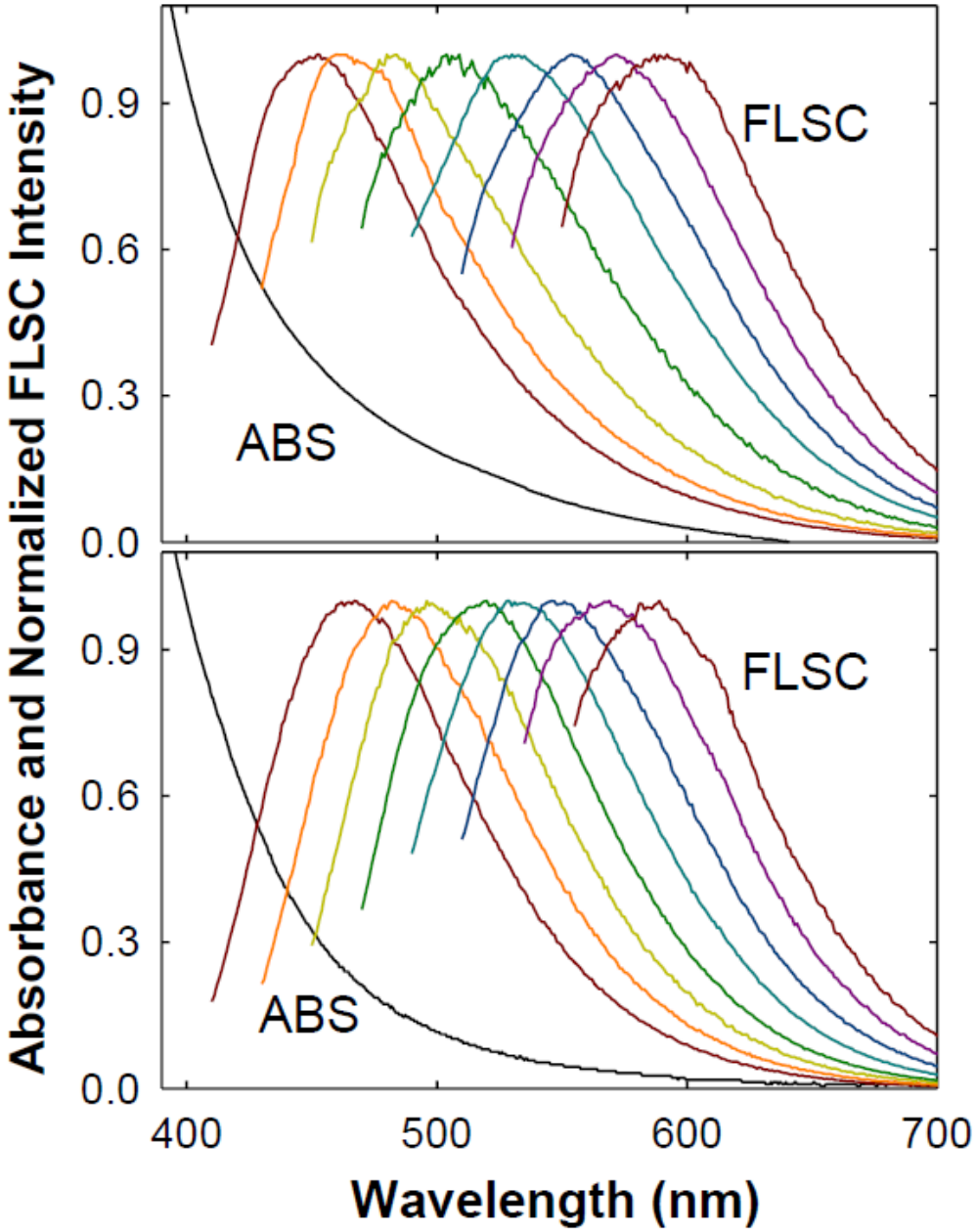


**Figure 3.** Absorption (ABS) and fluorescence (FLSC) spectra of NEC-CDots (upper) and EDA-CDots (lower), both in chlorobenzene. The excitation wavelengths were (corresponding to the FLSC spectra from left to right) 400 nm–560 nm in 20 nm increments.

A dilute solution of NEC-CDots was used for the preparation of specimen for transmission electron microscopy (TEM) imaging. In the preparation, a few drops of the sample solution were deposited onto silicon-coated copper grids, followed by the removal of solvent via evaporation. Representative TEM images of NEC-CDots are shown in Figure 4, with the dot sizes generally comparable with those of the small carbon nanoparticles (on the order of 5 nm in diameter) [35]. The individual dispersion of the dots in TEM

images is consistent with the expected sample morphology of discrete CDots, not the nanocarbon/organic composite-like morphology found in carbonization produced samples (the "hybrids") [25], again due to the known sharp contrast between dispassion factors of carbon nanoparticles and organic molecules such as NEC. Because of the very different dissipation factors, under the microwave processing conditions the small carbon nanoparticles could be heated selectively and efficiently for the hydrogen abstraction without any substantial carbonization of NEC molecules.

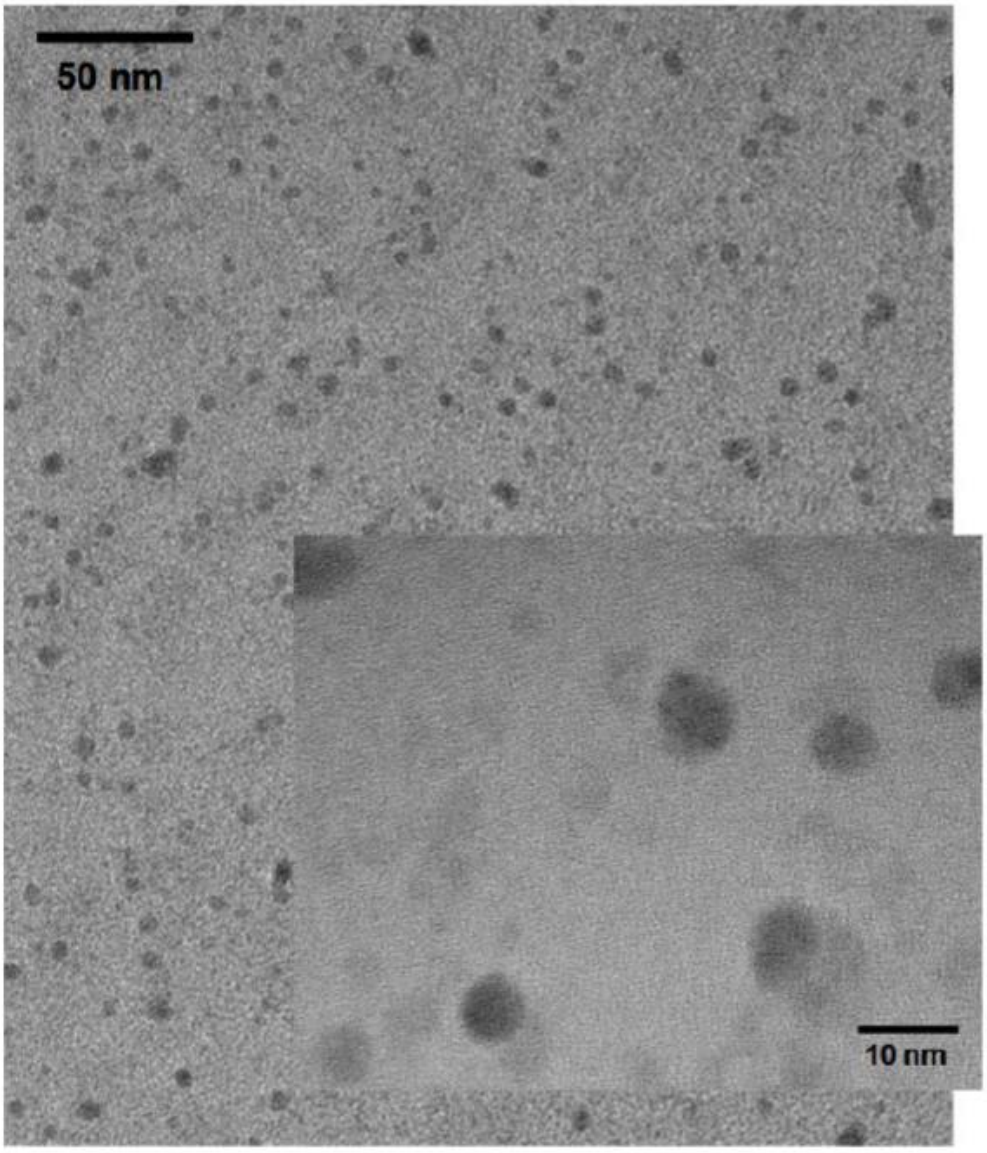


**Figure 4.** TEM images of NEC-CDots on silicon oxide coated copper grid, with those imaged at a higher resolution in the inset.

Atomic force microscopy (AFM) imaging results are also consistent with the sample morphology of mostly discrete NEC-CDots (Figure 5), significantly different from those of the "hybrids" obtained from the carbonization of organic precursors with microwave heating [25]. The dominating content of individual NEC-CDots in the dot sample is favorable to the more quantitative NMR characterization for structural elucidation of the dots, and conversely the success in the quantitative NMR measurements is in itself indicative of the sample morphology dominated by individually dispersed NEC-CDots.

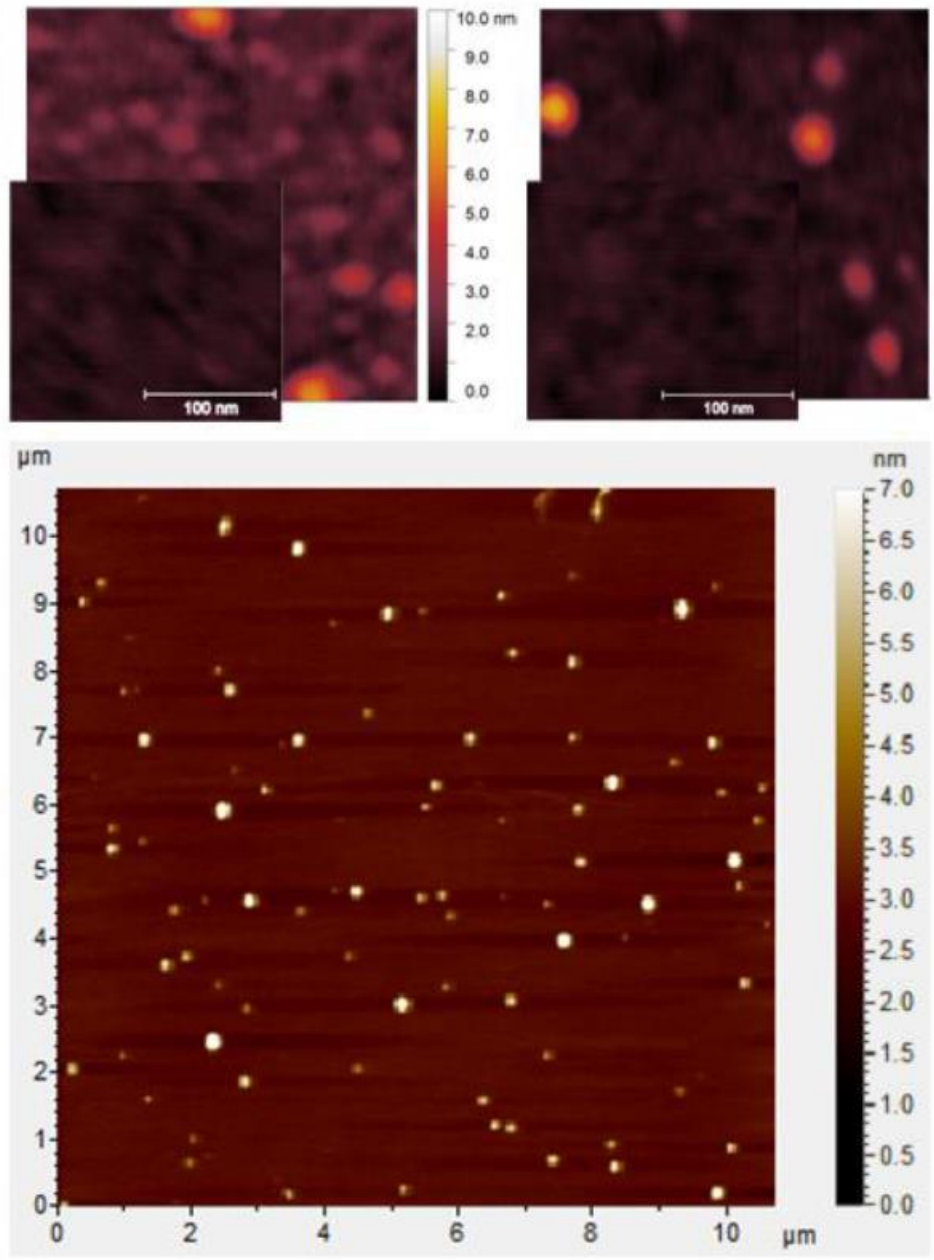


**Figure 5.** AFM images of NEC-CDots on silicon wafer (upper-right; inset: neat wafer) and on mica surface (lower) compared with those of the small carbon nanoparticles on silicon wafer (upper-left; inset: neat wafer). The upper images share the same height meter in the middle.

NEC-CDots are sufficiently soluble in common deuterated organic solvents for more quantitative solution-phase proton and $^{13}$C NMR measurements. Shown in Figure 6 is a comparison of the proton NMR results of NEC-CDots and free NEC molecules in DMSO-$d_6$. The signals due to NEC protons in the dot sample are obviously broader, consistent with the attachment of NEC species to the small carbon nanoparticles for the protons in varying environments. Despite the broadness, the integrations for the two aliphatic peaks are in the ratio of about 1-to-3 for the protons on the α-carbon to those on the β-carbon, clearly different from the ratio of 2-to-3 in free NEC. The same integration of all aromatic protons in whole is about 8, namely close to the 8-to-3 ratio of all aromatic protons to those on the β-carbon in free NEC. These more quantitative NMR results, again despite the signal broadening effect on the carbon nanoparticle-attached NEC species, support strongly the notion that there must be hydrogen abstraction at the α-carbon in NEC molecules (enabled

by the selective and efficient microwave heating of the carbon nanoparticles) [36–38] to generate radicals for in situ additions to the nanoparticles (Figure 2).

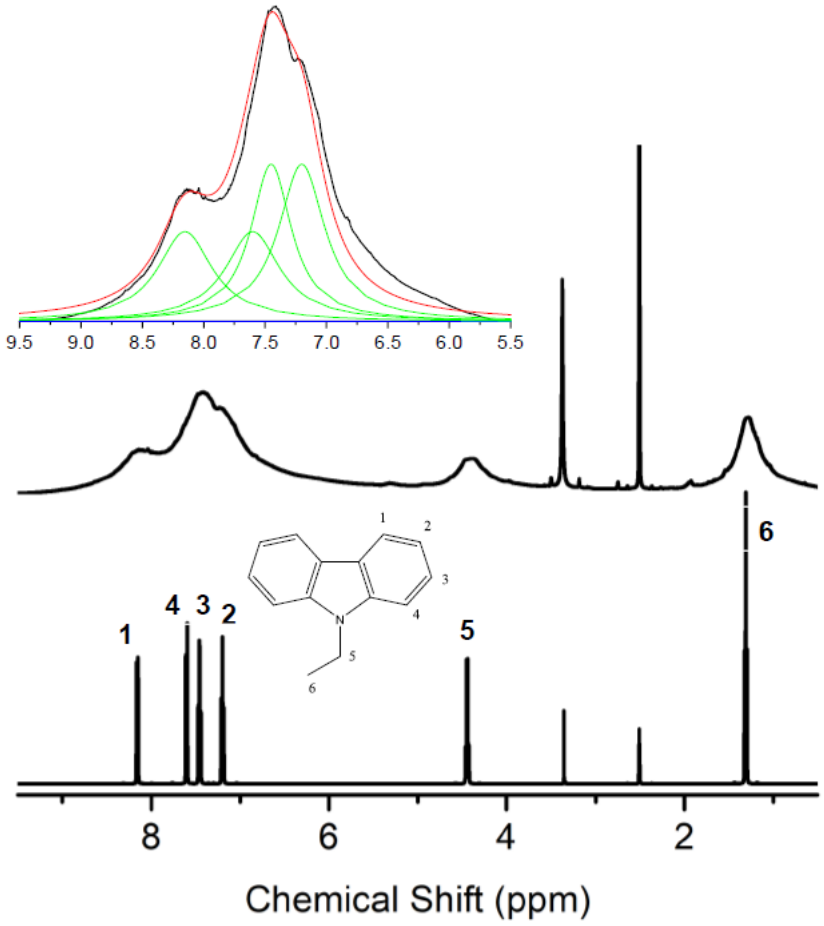


**Figure 6.** Proton NMR spectra of NEC-CDots (upper) and free NEC (lower), both in DMSO-$d_6$. The sharp peaks around 3.3 ppm and 2.5 ppm are due to water and DMSO, respectively. Inset: Results from the deconvolution via curve fitting of the aromatic signals with the assumption that the four peak maxima are unchanged from those in the free NEC.

Further effort was made to deconvolute the broad aromatic proton signals by curve-fitting with various assumptions and/or constraints, which were found necessary for the fact that the observed broad aromatic signals are composed of four severely overlapping peaks [39]. By assigning a Gaussian-Lorentzian function to each underlying peak [40], the aromatic signals over 9.5–5.5 ppm were fitted with the assumption of all four peak maxima unchanged from those of free NEC. The assumption represents a rough approximation, but the deconvolution results (Figure 6) seem reasonable, except for the obviously different integrations of the four deconvoluted peaks (protons 1,4,3,2 of integrations 1,1,1.3,1.5 in NEC-CDots versus all four protons of the same integration in free NEC). The deconvoluted four aromatic peaks are also all significantly broader than the two aliphatic peaks as measured by the peak full width at half maximum [FWHM in ppm for signals 1 (0.54), 4 (0.54), 3 (0.4), 2 (0.46), 5 (0.29), and 6 (0.29)] (Figure 6). A possible argument is that the interactions of the different aromatic protons with the attached carbon nanoparticle might be different, which could in principle alter the signal integrations, but the same argument would also seriously question the validity of the assumption led to the deconvolution results. Other assumptions and/or constraints were tried, including the constraint of the same width for all four peaks in addition to the assumption above (Supplementary Materials), but no improvements in terms of making the results more consistent with those of free NEC, which suggests the need for other experimental parameters to better define

the deconvolution via curve fitting. Ultimately a dedicated investigation to determine more precisely the structural arrangement of NEC species on the carbon nanoparticle surface is required.

On the $^{13}$C NMR results (Figure 7), the broad signals are generally consistent with the dot structural features discussed above on the basis of the proton NMR results. However, for the solubility limitation of the dot sample, the fact that the $^{13}$C NMR spectrum of NEC-CDots could be acquired with a 36 mg/mL solution of NEC-CDots in DMSO-$d_6$ and 10,000 scans is in itself interesting, which seems to suggest that the NEC carbons on the dot surface are not as inhomogeneous as one might anticipate. Additionally, interesting is that the aromatic carbon signals are significantly broader than the aliphatic ones (Figure 7), similar to what is reflected in the proton NMR results, which might be rationalized by the dot structure such that the carbazole aromatic plane is lying flat and close to the carbon nanoparticle surface (Figure 2). In such an individual dot structure, the aromatic moiety of the NEC species on the carbon nanoparticle surface must be contributing significantly to the effective passivation of nanoparticle surface defects via noncovalent interactions. Such interactions and their consequences in the surface passivation of carbon nanotubes were also investigated with similar outcomes, as reported in the literature [3,41].

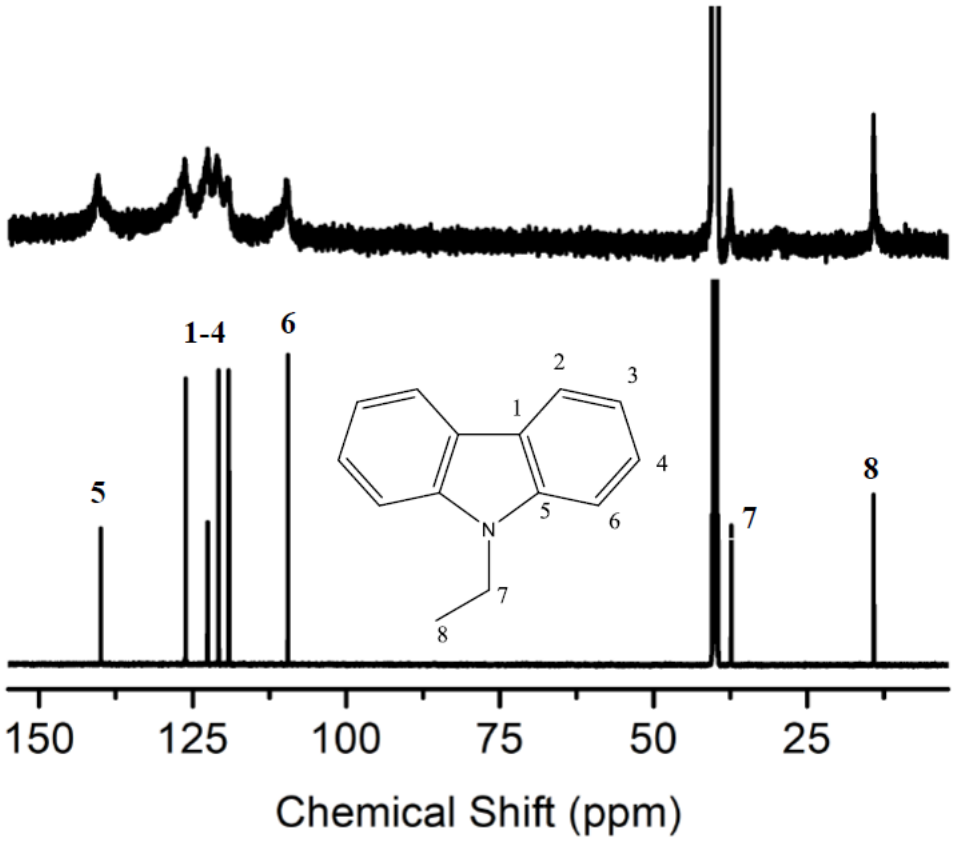


**Figure 7.** $^{13}$C NMR spectra NEC-CDots (upper) and free NEC (lower), both in DMSO-$d_6$.

The addition of NEC radials to carbon nanoparticles should form C-C linkages in the resulting NEC-CDots (Figure 2), analogous at least phenomenologically to additions of organic radicals to fullerenes and carbon nanotubes [29,42,43]. Unlike fullerenes that are stoichiometrically precise molecules, carbon nanotubes are known for their unavoidable structural defects, thus more comparable with small carbon nanoparticles. In fact, the defect sites on carbon nanotubes can be considered as nanoparticle-like [44], as the organic functionalized carbon nanotubes with their defect sites effectively passivated exhibit largely the same bright and color fluorescence emissions as those of CDots [41,45,46]. Among the carbons on nanotubes, those associated with or in the vicinity of the defects are generally

considered as being more active, thus more susceptible to derivatization including radical addition, namely a functionalized carbon on the nanotube is by itself a defect that drives further derivatization. This is manifested in the observed clustering of the introduced functional groups along the nanotube in the organic functionalized carbon nanotubes, with the clustered functional groups essentially cutting the nanotube surface into segments. Similarly for small carbon nanoparticles, the expectation should be that the radical additions are concentrated in the more defective areas of the nanoparticle surface, thus more favorable to the desired effective passivation of the nanoparticle surface defects, which represents the essence of carbon dots.

The expected C-C linkages in NEC-CDots with additions of NEC radicals to small carbon nanoparticles are consistent with the high stability of the dot sample, which is reflected by the observed stability in observed optical spectroscopic properties of the sample. For CDots prepared by the functionalization based on amidation chemistry of amines with the carbon nanoparticle surface-bound carboxylic moieties, the gradual reversal (or "defunctionalization") could be observed in the thermal treatment of the sample solution via refluxing, which is generally accompanied by progressively lower fluorescence emission intensities [28]. Similar evaluations on NEC-CDots for potential defunctionalization were performed by refluxing the dot sample in THF, toluene, and chlorobenzene solutions for up to 12 h, coupled with fluorescence quantum yield measurements in regular time intervals. The selection of the solvents was based on the consideration of their different polarities and their associated different refluxing temperatures representative of the upper temperature range for common uses of the dot samples. As shown in Figure 8, the variations in the observed fluorescence quantum yields from the average are mostly within 5%, which is typically the acceptable experimental uncertainty or variation to be expected with the determination of fluorescence quantum yields by the relative method [47,48]. The results demonstrate the high stability of NEC-CDots.

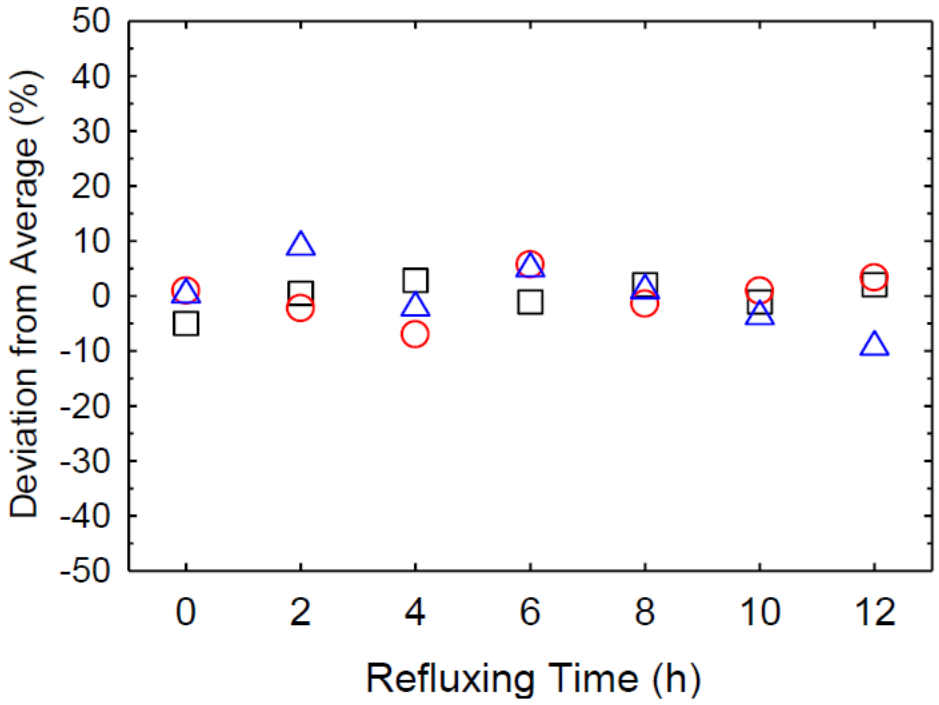


**Figure 8.** Evaluation on the sample stability based on the percentage deviation of observed fluorescence quantum yields from the average value after the dot sample was refluxed in THF (66 °C, circle), toluene (111 °C, square), and chlorobenzene (132 °C, triangle) for up to 12 h.

## 4. Summary and Conclusions

In the carbon dots research field, the dot samples are generally prepared by the deliberate chemical functionalization of preexisting small carbon nanoparticles, the same as the synthesis in which carbon dots were originally found, and by the thermal carbonization of organic precursors to create the nanoscale carbon entities mixed with organic species in "one-pot", thus with the sample morphology of essentially "nano-carbon/organic hybrids". For the former, the microwave treatment of small carbon nanoparticles dispersed by NEC molecules in the solid-state mixture represents an effective chemical functionalization approach, which takes advantage of the much larger microwave dissipation factor of carbon nanoparticles for their selective heating. The hot carbon nanoparticles are capable of hydrogen abstraction to create NEC radicals, the in situ addition of which to the nanoparticles yields NEC-functionalized small carbon nanoparticles, and thus NEC-CDots. The morphology of thus prepared dot sample dominated by individual NEC-CDots, not the composite-like morphology commonly found in the carbonization produced samples (including those with the use of microwave heating), is supported by the characterization results. Thus, a conclusion is that by selecting organic molecules of relatively active hydrogen(s), the microwave processing may be generalized as an effective and efficient approach for the functionalization of preexisting small carbon nanoparticles. The high quality of the dot samples thus produced in terms of the uniformity in the samples is reflected by the clean and more quantitative proton and $^{13}$C NMR results. As related, the mode of functionalization via C-C bonds that makes the CDots robust in structure and stable in properties also represents a major and unique advantage.

**Supplementary Materials:** The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/c9010005/s1, Details on the preparation of NEC-CDots, and alternative results from the deconvolution of aromatic proton NMR signals of NEC-CDots.

**Author Contributions:** Data acquisition and analyses, W.L., B.S., E.Y.C., W.C., L.P., P.W., L.C. and A.S.; Funding acquisition, L.Y. and Y.-P.S.; Investigation, W.L. and B.S.; Project administration, C.E.B., L.Y. and Y.-P.S.; Supervision, C.E.B. and Y.-P.S.; Validation, W.L. and B.S.; Writing—original draft, W.L., B.S., P.W. and Y.-P.S.; Writing—review and editing, C.E.B., L.Y. and Y.-P.S. All authors have read and agreed to the published version of the manuscript.

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**Conflicts of Interest:** The authors declare no conflict of interest.

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