

# Photoexcited State Properties of Poly(9-vinylcarbazole)-Functionalized Carbon Dots in Solution versus in Nanocomposite Films: Implications for Solid-State Optoelectronic Devices

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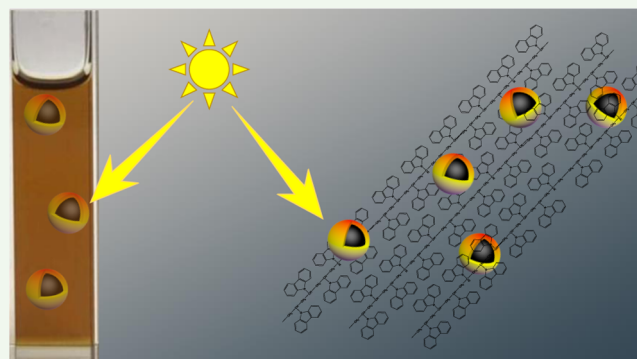


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Supporting Information

**ABSTRACT:** Carbon dots (CDots) are small carbon nanoparticles with effective surface passivation accomplished mostly via organic functionalization. In this study, the largely amorphous carbon nanoparticles were copolymerized with *N*-vinylcarbazole in microwave-assisted radical reactions. The copolymers thus formed are structurally equivalent to the individual carbon nanoparticles each surface-functionalized by multiple poly(*N*-vinylcarbazole) (PVK) segments, thus denoted as PVK-CDots. Their electronic transitions and photoexcited state properties, including especially the characteristic excitation wavelength dependencies of fluorescence parameters, were found to be essentially the same as those commonly observed in CDots of small organic molecules for surface functionalization. The PVK-CDots were dispersed in neat PVK for polymeric nanocomposite films free from any other foreign materials. The optical absorptions and fluorescence emission properties of PVK-CDots in the solid-state film matrix environment were found to be little changed from those in solution. The significance of the findings and implications to various uses of these nanomaterials in optoelectronics and related fields are highlighted and discussed.



**KEYWORDS:** carbon dots, poly(*N*-vinylcarbazole), copolymerization, optical absorption, fluorescence emissions, nanocomposite films

## INTRODUCTION

Functionalized carbon nanostructures, especially those with optoelectronically important polymers such as polythiophenes and poly(*N*-vinylcarbazole) (PVK) for functionalization, have been widely pursued for their uses in various devices, with applications ranging from sensing to solar energy conversion and to optical displays.<sup>1–4</sup> The functionalization has included both covalent and noncovalent modes or configurations.<sup>1,5</sup> For example, fullerenes as electron-deficient molecules were incorporated into PVK polymers of well-established hole transport characteristics for the resulting materials to be used as photoconductors.<sup>6,7</sup> Carbon nanotubes were functionalized by poly(3-hexylthiophene) (P3HT),<sup>8</sup> with the derived composites found to perform significantly better than the P3HT in organic field-effect transistors.<sup>9,10</sup> Generally, for the different nanoscale carbon allotropes, including fullerenes, carbon nanotubes, and graphene nanosheets, their modifications by or their coupling with optoelectronically important polymers in various structural configurations represent a highly active research field.<sup>11–14</sup>

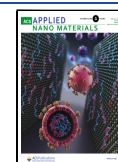
More recently, small carbon nanoparticles that are generally without any defined crystal structures have been found to

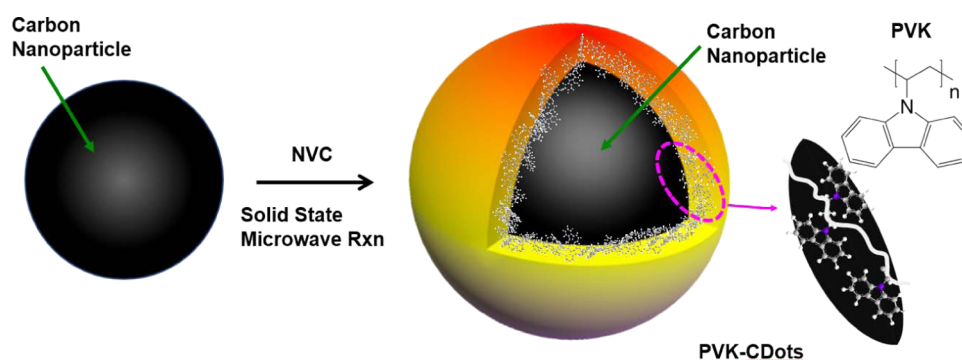
possess excellent photon-harvesting capabilities and also rich photoinduced properties and processes.<sup>15–18</sup> In fact, there is growing experimental evidence suggesting that these carbon nanoparticles of a few nanometers in size may better represent the nanoscale carbon allotrope at zero-dimension.<sup>19–22</sup> As a unique attribute associated with their largely random amorphous structure and dot-like size, the carbon nanoparticles are populated with abundant defect sites, especially on the particle surface. Consequently, the defect sites on the carbon nanoparticles may serve as energy traps following photoexcitation, even though the lifetimes of the trapping sites appear rather short. The analogous phenomenon was also found in the study of defective carbon nanotubes, which should not be surprising because carbon nanotubes of structural and end defects could be considered as being

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**Figure 1.** Cartoon illustration of the PVK-functionalized small carbon nanoparticle, denoted as PVK-CDots, from the microwave-assisted radical copolymerization of *N*-vinylcarbazole (NVC) with small carbon nanoparticles harvested from carbon soot.

equivalent to the nanotubes decorated with small carbon nanoparticles.<sup>19,21</sup> The defect sites on carbon nanotubes were used for the chemical functionalization of the nanotubes, which was accompanied by the interesting finding that the functionalized carbon nanotubes could exhibit bright visible fluorescence emissions,<sup>23–25</sup> completely different from the band gap fluorescence found and reported a few years later.<sup>26–28</sup> The visible fluorescence in the functionalized carbon nanotubes was attributed to the emissive excited states associated with the energy trapping defect sites that might be stabilized by the passivation effects due to the chemical functionalization.<sup>23–25</sup> The same functionalization was applied to small carbon nanoparticles, which resulted in the finding of carbon “quantum” dots or carbon dots (CDots, Figure 1).<sup>15,16,19</sup> In addition to their intense and multicolor fluorescence emissions, CDots have been explored for their unique/advantageous photoexcited state properties and redox characteristics, with their actively pursued technological applications across all those commonly targeted by the use of traditional molecular dyes, conventional semiconductor quantum dots, and other photoactive nanomaterials.<sup>19,29–39</sup>

Most spectroscopic and other investigations of CDots have been in solutions, though many targeted applications of the dots are in polymeric composites and various other solid-state material configurations. For nanocomposite films of CDots with a selected polymer, typically preprepared CDots are mixed well with the polymer for wet casting or extrusion.<sup>40</sup> However, in the development of polymeric nanocomposites in which the fillers are functionalized carbon nanomaterials, it is generally more desirable to have the matrix polymers for the functionalization of the carbon nanomaterials so as to eliminate any other molecules/agents as “foreign materials” in the resulting nanocomposites. Such an approach is particularly valuable to nanocomposites of optoelectronically significant polymers.<sup>41</sup> Thus, for PVK/CDots nanocomposite films in this work, the preprocessed and selected small carbon nanoparticles were copolymerized with *N*-vinylcarbazole in microwave-assisted reactions to yield copolymers in which the carbon nanoparticles are surface-functionalized by PVK, a configuration matching that of the classically defined CDots (Figure 1), thus denoted as PVK-CDots. The dot sample could readily be mixed with blank PVK polymers for the fabrication of neat nanocomposite films containing only the small carbon nanoparticles and PVK, without any other foreign substances. The photoexcited state properties of PVK-CDots in solution and in the neat nanocomposite films were investigated and compared. The results and their implications to the use of

CDots in polymeric nanocomposites for optoelectronic and other applications are discussed.

## EXPERIMENTAL SECTION

Experimental details the same as or similar to what were reported previously are provided in the Supporting Information. The harvesting of small carbon nanoparticles from the commercially acquired carbon nanopowders followed a protocol similar to what was reported previously (see also Supporting Information for a typical transmission electron microscopy (TEM) image).<sup>40</sup> Highlighted below is the preparation of PVK-CDots via the copolymerization reaction.

For the reaction, a mixture of the nanoparticle sample (70 mg) with NVC (500 mg) was prepared by grinding, followed by the dispersion in tetrahydrofuran (THF) (5 mL) via sonication (VWR 250D bath sonicator). The dark-colored dispersion was stirred for 12 h and then evaporated to remove THF to obtain a solid-state mixture of the carbon nanoparticles and NVC. Separately, a solid-state bath of silicon carbide powders (150 g) in a silica crucible casting dish was heated in a conventional microwave oven at 500 W for 3 min. The scintillation vial containing the carbon nanoparticles-NVC mixture was immersed in the solid-state bath for microwave irradiation at 500 W for about 3 min. The treated mixture was removed from the oven and cooled to ambient temperature, ground for about 10 min, and then put back into the silicon carbide bath in the oven for microwave irradiation at 500 W for 3 min. The same procedure was repeated three more times, and in the later two times, the microwave irradiation was at 700 W for 3 min. Then, the reaction mixture was dispersed in toluene (5 mL) with vigorous sonication, and centrifuged at 20 000g to discard the sediment. The supernatant was precipitated into hexane (25 mL) as the antisolvent to collect the precipitates. They were then dispersed in toluene, followed by centrifuging at 20 000g to collect the dark-colored supernatant as a toluene solution of the PVK-carbon nanoparticles copolymers denoted as PVK-CDots.

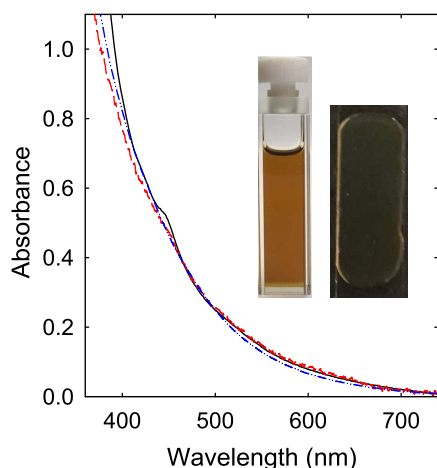
## RESULTS AND DISCUSSION

The PVK-CDots samples in this study were prepared using pre-existing small carbon nanoparticles for their surface functionalization with PVK in the copolymerization reaction. The growing experimental evidence has suggested that such samples, whose preparation is commonly regarded in the literature as the deliberate chemical functionalization synthesis for the dot structure illustrated in Figure 1, are considerably different from those dot samples obtained from the popular “one-pot” thermal carbonization of organic matters as precursors.<sup>22,42–45</sup> The focus of this study was on the former only.

The processing of the commercially supplied carbon nanopowders is facile and established, yielding small carbon nanoparticles (average around 5 nm in diameter, largely

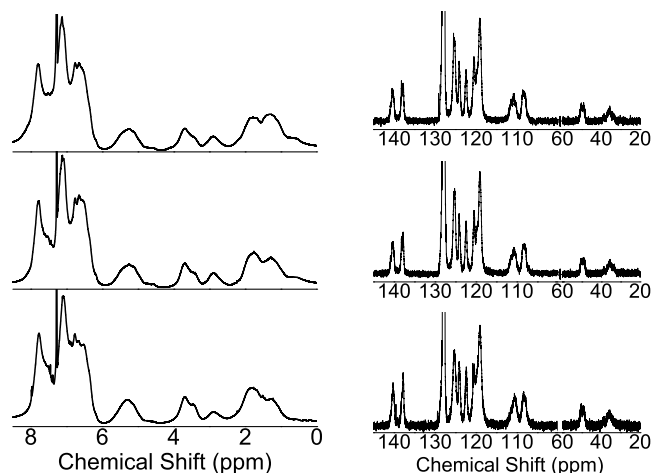
amorphous, no defined X-ray diffraction peaks).<sup>46</sup> For the nanoscale sizes of the particles and the conditions used in their processing, it should be expected that the particle surface is populated by abundant defect sites. In fact, it is the effective passivation of such defects that is responsible for the observed photoexcited state properties of CDots (Figure 1).

The small carbon nanoparticles were functionalized in the microwave-assisted copolymerization reaction with *N*-vinylcarbazole (NVC). For the reaction, a solid-state mixture of the small carbon nanoparticles carefully dispersed in NVC was prepared. The mixture was treated in a conventional microwave oven with the protocol and conditions designed to impart thermally induced copolymerization reaction, but at the same time not to cause any significant carbonization of the NVC molecules and their derived species. It is known that the heating of vinyl compounds in general and NVC in particular results in polymerization reactions.<sup>47</sup> In this study, microwave irradiation is equivalent to rapidly heating the reactants and, moreover, the heating is concentrated more on the carbon nanoparticles for their high microwave cross sections.<sup>48</sup> Thus, while the reaction is conceptually similar to the thermally initiated copolymerization in mixtures of the small carbon nanoparticles with NVC at elevated temperatures, a key difference with the heating by microwave irradiation is that it targets more selectively the small carbon nanoparticles to impart more reactions around the nanoparticles and correspondingly the desired more surface functionalization of the nanoparticles in the resulting copolymers. The copolymers from the reaction of the small carbon nanoparticles with NVC are denoted as PVK-CDots. After the copolymerization, the reaction mixture was cleaned via repeated precipitations from toluene into hexanes, followed by vigorous centrifugation in toluene to keep the highly colored supernatant as a toluene solution of PVK-CDots. For spectroscopic measurements, toluene was evaporated, and the resulting solid PVK-CDots sample was dissolved in dimethylformamide (DMF) at 50 °C (water bath). The optical absorption spectrum of PVK-CDots in solution is similar to that of the aqueous suspended small carbon nanoparticles (Figure 2), as expected. The control sample from the reaction of neat NVC under the same processing conditions is colorless, also as expected.



**Figure 2.** Optical absorption spectra of PVK-CDots in DMF solution (solid) and in PVK thin film (dash) and aqueous suspended small carbon nanoparticles (dash-dot-dot). Inset: photos of solution (left) and film of PVK-CDots in PVK (right).

The polymeric nature of PVK-CDots and the blank PVK without carbon nanoparticles was confirmed in <sup>1</sup>H NMR measurements. In the experiment for using the established end-group analysis method to estimate the PVK polymer average molecular weight,<sup>49,50</sup> <sup>1</sup>H NMR spectra of PVK-CDots in deuterated chloroform solution were acquired. The proton signals thus obtained (Figure 3) are rather broad, thus making



**Figure 3.** <sup>1</sup>H (left) and <sup>13</sup>C (right) NMR spectra of PVK-CDots (upper), PVK polymers obtained by the same microwave processing of NVC only without carbon nanoparticles (middle), and the PVK polymers acquired commercially (lower).

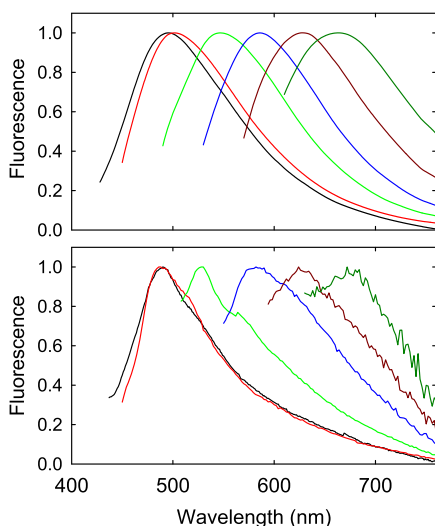
a determination of the end group signal shifts impossible. In the end-group analysis, the signal shifts serve as the basis for estimating molecular weight, and the failure due to the signals being too broad suggests that the sample is too polymeric, beyond the limit of the analysis. Nevertheless, some valuable information may still be extracted on the molecular weight range of the polymers. Since the generally accepted molecular weight upper limit based on <sup>1</sup>H NMR end group signal shifts is ~25 000, it may be reasonable to have that as the lower end of the estimated molecular weight ( $M_n$ ) for PVK polymers in the dot sample.<sup>50</sup> This estimate may be further supported by the comparison between <sup>1</sup>H NMR spectra of the commercial PVK polymers ( $M_n \sim 90\,000$ ), PVK-CDots, and the blank PVK in Figure 3. They are all similarly very broad.

The NMR results of the dot sample solution are obviously dominated by PVK polymers because the content of carbon nanoparticles in the soluble sample is relatively low, on the order of 10% by weight based on estimates of thermogravimetric analysis (TGA) and also the optical absorbance with the known absorptivity of the suspended small carbon nanoparticles, which takes advantage of the fact that PVK is colorless (absorption spectrum of neat PVK provided in the Supporting Information), and the observed optical absorptions in the visible spectral region are due entirely to carbon nanoparticles in the dot sample (Figure 2).<sup>17,33</sup>

In microwave irradiation, the carbon nanoparticles for their high microwave cross sections are heated preferentially to serve the initiator-like function for the radical copolymerization with NVC so that the nanoparticles are covalently incorporated in the copolymer structure. In such a structural configuration, effectively, the surface of each carbon nanoparticle is passivated by a combination of the covalently attached PVK segments and the noncovalent interactions with the carbazole moieties, thus

following the general definition on CDots (Figure 1). In comparison with the same copolymerization reaction by heating without microwave irradiation, for which a high temperature like 350 °C is generally needed to limit the degree of polymerization and the associated formation of mostly insoluble materials,<sup>20</sup> the microwave irradiation offers significant advantages, including higher efficiency and more reactions around the carbon nanoparticles for more effective passivation of the surface defects, thus higher fluorescence emission quantum yields.<sup>19,51</sup> The observed high fluorescence quantum yields of the dot sample (around 25% at 400–420 nm excitation) also serve to exclude the possibility that the carbon nanoparticles and PVK polymers were simply mixed in the sample because without the strong interactions due to the copolymer structures in the simple mixture of the small carbon nanoparticles with blank PVK polymers, the observed fluorescence quantum yields were much lower (only about 1.5% for excitation at 400 nm).

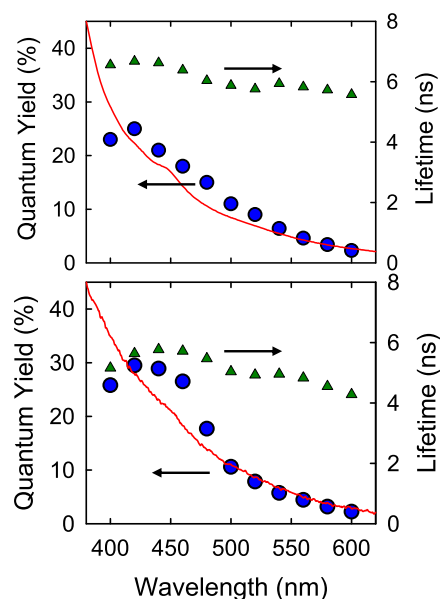
As in other CDots, the fluorescence spectra and quantum yields of PVK-CDots in solution are dependent on excitation wavelengths in rather characteristic patterns.<sup>52</sup> For excitations at progressively longer wavelengths, the fluorescence spectra red-shift progressively (Figure 4), which are correlated with



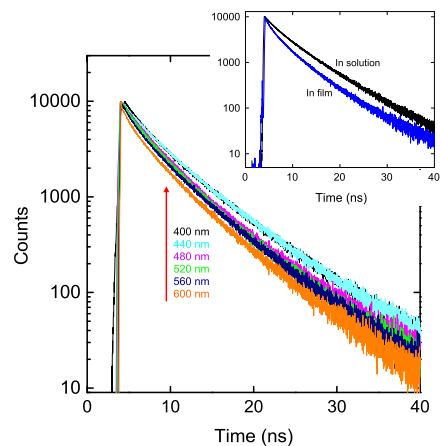
**Figure 4.** Fluorescence spectra of PVK-CDots in DMF solution (upper) and in PVK thin film (lower) with progressively longer excitation wavelengths (from left to right) of 400, 440, 480, 520, 560, and 600 nm.

progressively lower quantum yield values (Figure 5). However, the observed decays of fluorescence are much less sensitive to excitation wavelengths (Figure 6), generally with the longer excitation wavelengths corresponding to only slightly faster decays (Figure 6). All of the decays are non-exponential but not too far from linear on the log scale (Figure 6), and they can all be deconvoluted using the bi-exponential function, which represents the averaging of multiple decay processes. In a further averaging, the two fluorescence lifetimes ( $\tau_{F1}$  and  $\tau_{F2}$ , with the corresponding  $A_1$  and  $A_2$ ) obtained from fitting the decay curves (Figure 6) can be fed into the equation  $\langle\tau_F\rangle = (A_1\tau_{F1}^2 + A_2\tau_{F2}^2)/(A_1\tau_{F1} + A_2\tau_{F2})$ ,<sup>53</sup> where  $\langle\tau_F\rangle$  is the average lifetime at the selected excitation wavelength (Figure 5).

The excitation wavelength dependencies of fluorescence emission spectra, quantum yields, and decays (average lifetimes) shown in Figures 4–6 for PVK-CDots in solution

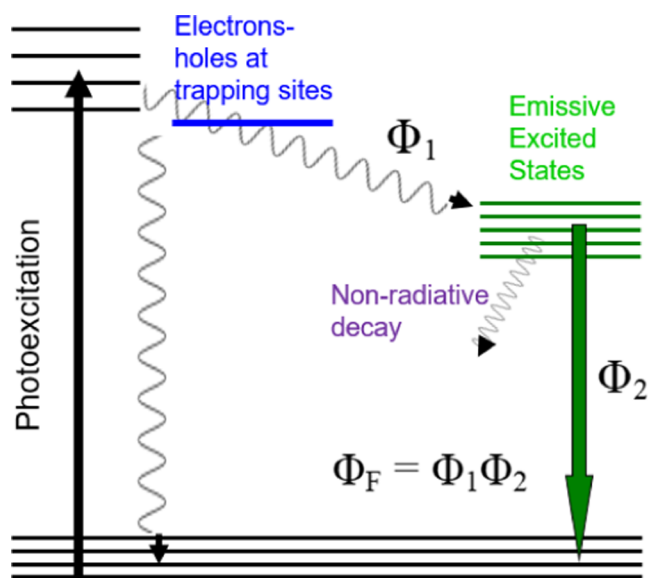


**Figure 5.** For PVK-CDots in DMF solution (upper) and in PVK film (lower), the observed fluorescence quantum yields ( $\Phi_F$ , circle) and averaged fluorescence lifetimes ( $\langle\tau_F\rangle$ , solid triangle) at different excitation wavelengths. The corresponding absorption spectra (solid lines) are also shown.



**Figure 6.** Observed fluorescence decays of PVK-CDots in DMF solution at the indicated excitation wavelengths (with the arrow showing the progressively and slightly increasing counts around 10 ns from 600 nm excitation to the similar 440 and 400 nm excitations). Inset: a comparison between decays in solution and in film at 420 nm excitation.

are rather similar to those reported previously for CDots with small amine molecules for the carbon nanoparticle surface functionalization,<sup>15,52,54</sup> suggesting largely the same photoexcited state properties and processes. Mechanistically on CDots in general,<sup>19</sup> the photoexcitation of small carbon nanoparticles in the dots drives rapid charge transfers and separation for electrons and holes, which are trapped at the nanoparticle surface defect sites stabilized by the passivation associated with the organic functionalization (Figure 1). The radiative recombination of the separated redox pairs results in emissive excited states that are responsible for the observed bright and colorful fluorescence emissions. Mechanistically, in such a framework (Figure 7), the experimentally observed decoupling in the excitation wavelength dependence

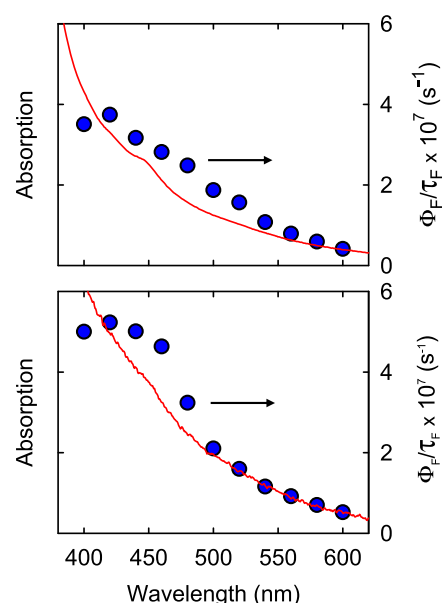


**Figure 7.** Mechanistic framework for the photoexcited state processes of CDots. The radiative recombinations for the formation of the emissive excited states (with the yield  $\Phi_1$ ) are very fast, within the sub-nanosecond time resolution of the instrument in this work for the fluorescence rise time. Thus, the experimental fluorescence decays capture only the deactivation of the emissive excited states (with the yield  $\Phi_2$ ), and the observed fluorescence quantum yields ( $\Phi_F$ ) capture everything.

fluorescence yields and average fluorescence lifetimes, as shown in Figure 5, might be due to the quantum yields and decays capturing different photoexcited state processes. The former is a combination of yields for both the formation and deactivation of the emissive excited states ( $\Phi_F = \Phi_1\Phi_2$  in Figure 7), whereas the latter is for the deactivation only because the fluorescence rising corresponding to the formation of the emissive excited states is obviously on a much shorter time scale than that for the decays (Figure 6).

In the absence of separate quantifications of  $\Phi_1$  and  $\Phi_2$ , which is rather difficult experimentally, an alternative to the discussion above is to assume  $\Phi_1 = 1$ , thus  $\Phi_F = \Phi_2$ , and the  $\Phi_F$  and  $\langle\tau_F\rangle$  both become associated with only the deactivation of the emissive excited states. Consequently, the above-discussed decoupling can only be attributed to the excitation wavelength dependence of fluorescence radiative rate constants ( $k_F = \Phi_F/\langle\tau_F\rangle$ ), which apparently coincides with the absorption profile of PVK-CDots (Figure 8). Since the optical absorptions of CDots are largely the same as those of the small carbon nanoparticles and they are generally considered as a distribution of electronic transitions, one may speculate, logically perhaps, that the progressively decreasing absorptivities at longer wavelengths may be correlated with decreasing transition probabilities and similarly the decreasing  $k_F$  values (Figure 8). Interestingly, essentially the same spectroscopic observations and analyses are shared between PVK-CDots and other CDots of small molecules or oligomers for surface functionalization,<sup>52</sup> thus again suggesting that CDots in general possess rather similar and characteristic photoexcited state properties and processes.

The absorption and fluorescence emission properties of PVK-CDots were investigated in thin films for a comparison of the results with those in solution. The films were prepared by mixing the dot sample with blank PVK, thus without any other



**Figure 8.** For PVK-CDots in DMF solution (upper) and in PVK film (lower), the calculated  $\Phi_F/\langle\tau_F\rangle$  ratios at different excitation wavelengths. Also shown are the corresponding absorption spectra.

foreign substances in the films, which appeared transparent with a light color. The color was due entirely to PVK-CDots in the films, with the observed absorption spectrum largely the same as that in solution (Figure 2). The results suggest that the wavelength distribution of electronic transitions in the small carbon nanoparticles responsible for the absorptions is little changed not only with the PVK functionalization but also from solution to the film environment. Interestingly, however, while fluorescence emission spectra of PVK-CDots in the films are still excitation wavelength-dependent, the spectral profiles and positions are somewhat different from those in solution (Figure 4). Such differences were mostly absent for the small diamine-functionalized CDots embedded in the poly(vinyl alcohol) (PVA) film matrix.<sup>40</sup> Since those hydrophilic CDots with small diamine molecules for surface functionalization are not compatible with PVK, it is difficult to make a more direct experimental comparison. Nevertheless, it is possible that the PVK functionalization accompanied by potentially significant interactions between carbazole moieties and the carbon nanoparticle surface in PVK-CDots might be different from the solution phase to the film matrix environment to alter somewhat the emissive excited states and the associated fluorescence emission profiles.

Fluorescence quantum yields of PVK-CDots in the films are similarly excitation wavelength-dependent, following largely the same pattern as that in solution (Figure 5). Also similar is the excitation wavelength dependence of the average fluorescence lifetimes ( $\langle\tau_F\rangle$ ) estimated from the same deconvolution of the observed decays using the bi-exponential decay function (Figure 5), though the actual  $\langle\tau_F\rangle$  values are generally somewhat smaller in the films than in solution (Figure 5), consistent with the observed faster decays in the films (Figure 6). Thus, the calculated  $k_F$  ( $\Phi_F/\langle\tau_F\rangle$ ) values are generally somewhat larger in the films (Figure 8), which is probably due in the most part to the increase in the reflective index ( $n$ ) from DMF solution to the PVK film matrix. The established photophysical principle calls for an  $n^2$  dependence of  $k_F$ , namely  $k_{F,\text{film}}/k_{F,\text{solution}} = (n_{\text{film}}/n_{\text{solution}})^2$ ,<sup>53</sup> even though

experimentally, the effect due to the change in reflective index has often been found to deviate from the more extreme  $n^2$  dependence. Nevertheless, the effect is real and well established in the literature,<sup>53</sup> and it could probably account for the observed larger  $k_F$  ( $\Phi_F/\langle\tau_F\rangle$ ) values in PVK films than those in DMF solution (Figure 8).

The comparison of fluorescence emission properties in solution versus in the PVK film matrix presented and discussed above suggests no significant differences, which should be very positive to the development of CDots-based/derived materials for uses in the solid state. More specifically, PVK is widely used for hole transport in optoelectronic devices, and CDots are pursued for various functions in many of the same devices. These should benefit significantly from the experimental confirmation that PVK-CDots in solid-state composite films retain the same optical and photoexcited state characteristics, which have been systematically investigated in the solution phase and thus more established. Beyond optoelectronics, the ability to incorporate small carbon nanoparticles into polymeric matrices via copolymerization opens up opportunities broadly in the development and preparation of nanocomposite materials for a variety of applications. Furthermore, the participation of the small carbon nanoparticles in the radical copolymerization reactions with vinyl molecules is also very significant, demonstrating that they are similar to fullerenes for radical scavenging and more broadly amenable to surface modifications by organic radicals for derivatizations,<sup>46</sup> which may substantially expand the usage of small carbon nanoparticles.

## CONCLUSIONS

The results reported here suggest that small carbon nanoparticles are capable of participating in radical copolymerization reactions with *N*-vinylcarbazole, for which microwave irradiation for more efficient and targeted heating is advantageous. Structurally, the copolymers thus formed may be complex, similar to the copolymers of fullerenes with vinyl molecules, including *N*-vinylcarbazole, but an educated speculation is such that these polymers are branched with each carbon nanoparticle connecting/crosslinking multiple PVK segments, namely, locally individual carbon nanoparticles are each surface-functionalized by the multiple PVK segments. Such a structural configuration is equivalent to that in the classically defined CDots, thus the designation of the copolymers as PVK-CDots. Indeed, the observed optical absorption and fluorescence emission properties of the copolymers, in which the small carbon nanoparticles are surface-passivated effectively via the PVK functionalization, are essentially the same as those found in many other CDots with the surface functionalization by small molecules. The results not only justify the PVK-CDots designation but also demonstrate the highly consistent and characteristic nature of the electronic transitions and photoexcited state properties and processes in CDots with small molecular and polymeric surface functionalities. Also significant is the experimental confirmation in this work that the optical absorptions and photoexcited state properties of PVK-CDots are little changed from solution phase to film matrix in solid state, which makes these nanomaterials more valuable to applications in optoelectronics and related technologies.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsnm.1c04560>.

Experimental details, materials, and measurements; TEM image; PVK absorption spectrum in DMF, and table of TCSPC parameters (PDF)

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### Notes

The authors declare no competing financial interest.

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