Glycothermally Synthesized Carbon Dots with Narrow-Bandwidth and Color-Tunable Solvatochromic Fluorescence for Wide-Color-Gamut Displays

Taishu Yoshinaga, Momoka Shinoda, Yoshiki Iso,* Tetsuhiko Isobe,* Akihiro Ogura, and Ken-ichi Takao

ABSTRACT: Fluorescent carbon dots (CDs) represent a promising eco-friendly next-generation phosphor. However, most CDs exhibit broad photoluminescence (PL) spectra [full width at half-maximum (fwhm) over 60 nm]; few works on CDs with sharp PL spectra (fwhm less than 40 nm) have been reported. In addition, their syntheses and color tuning require harsh conditions of high temperatures, long reaction times, and high pressures with catalysts. Here, we successfully prepared narrow-bandwidth emissive CDs (fwhm of 27−40 nm) from phloroglucinol in a glycol solvent of 1,2-pentanediol at temperatures as low as 180 °C for a reaction duration of as short as 6 h under ambient conditions without any catalysts via an open reaction system in which dehydration and condensation reactions among phloroglucinol molecules were enhanced. We shifted the emission peak from 463 to 511 nm by selecting seven kinds of solvents with different polarities, that is, emission colors could be tuned from blue to green by taking advantage of fluorescence solvatochromism. The CD-dispersed polymer films showed a similar solvatochromic behavior and sharp PL spectra, verifying the feasibility of applying the CDs to displays with a wide color gamut.

INTRODUCTION

Phosphors are used in a wide variety of applications, such as lighting, displays, solar cells, and medical probes that are vital for society. Fluorescent carbon nanoparticles, called carbon dots (CDs), were discovered in 2004 and have received a great deal of attention as next-generation phosphors.1−10 CDs can be produced from a variety of organic materials and possess robust graphite structures, contributing to their environmental friendliness, high thermal stability, and high photostability.4,8,9 Because of these favorable characteristics, CDs are expected to serve as alternatives to quantum dots (QDs) of CdSe/ZnS and CsPbX3 (X = Cl, Br, and I) containing the toxic elements Cd and Pb and organic dyes. CDs have been applied in bioimaging,1,11,12 sensors for heavy metals,13,14 thermal sensors,15,16 and LEDs.16,17

The photoluminescence (PL) properties of CDs have been improved through the scrutiny of organic materials and the optimization of synthesis conditions and purification processes. Accordingly, the preparation of multicolor CDs with high PL quantum yields (QYs) has been reported.9,18,19 However, the PL spectra of CDs are usually broad, and their full widths at half-maximum (fwhms) exceed 60 nm,16,20,21 resulting in low emission color purity. The emission color purity is higher when the distribution of emission wavelengths, that is, the emission peak width, is narrower. There have been remarkably few reports on visible light-emissive CDs with fwhms less than 40 nm (Table 1). In contrast, QDs exhibit high color purity, with fwhms less than 30 nm (Table S1). To apply CDs to wide-color-gamut displays, it is desired to improve their color purity in the visible region.

The excitation-dependent broad-bandwidth emissive CDs have been produced through the pyrolysis and carbonization of organic materials. They contain different particle sizes and a variety of surface functional groups,10,19,29 therefore, they have diverse energy gaps and surface trap levels depending on their particle size distribution and surface functional groups, respectively, resulting in excitation-dependent broad-bandwidth emission.10,19,29

In recent years, excitation-independent emissive CDs have been prepared through polymerization of aromatic organic molecules such as phloroglucinol (Ph) and phenylenediamine.23,26,30 For example, Yuan et al. reported that blue-
Bandwidth Emissive CDs

The size of the homogeneous surface hydroxy groups. They demonstrated that graphene structure of the CDs with a uniform size and narrow-bandwidth emission originated from the triangular wavelengths, a longer heating duration or the use of a

increase the size of the structure to achieve longer emission from blue emission to green and red emission. However, to molecular orbital (LUMO) and thus leading to a change molecular orbital (HOMO) and the lowest unoccupied in a reduction in the energy gap between the highest occupied through the dehydration and condensation reactions, resulting methane and petroleum ether in the puri

purify the CDs and used the harmful substances dichloro-

These authors performed silica column chromatography to of a Ph ethanol solution at 200 °C for 9 h (Scheme S1).25 The

emission color can be controlled by tuning the CD size due to the quantum size e

emitting CDs with an emission spectrum fwhm of 30 nm were produced via dehydration and condensation reactions between the OH groups of Ph molecules upon solvothermal treatment of a Ph ethanol solution at 200 °C for 9 h (Scheme S1).25 These authors performed silica column chromatography to purify the CDs and used the harmful substances dichloromethane and petroleum ether in the purification.25,26 The narrow-bandwidth emission originated from the triangular graphene structure of the CDs with a uniform size and homogeneous surface hydroxy groups. They demonstrated that the size of the π-conjugated graphene structure was increased through the dehydration and condensation reactions, resulting in a reduction in the energy gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) and thus leading to a change from blue emission to green and red emission. However, to increase the size of the structure to achieve longer emission wavelengths, a longer heating duration or the use of a dehydration catalyst involving additional purifications was required.25,26

To prepare narrow-bandwidth emissive CDs at lower temperatures, with a shorter heating duration, and without high pressure and any catalysts, we focused on designing an open reaction system using a high-boiling solvent rather than the closed reaction system in an autoclave used in the previous reports (Table 1), because the dehydration and condensation reactions are expected to be promoted by removing water from the system. Actually, we demonstrated that CDs with higher photoluminescence quantum yields (PLQYs) were produced when these reactions were performed in an open system with a nonaqueous solvent possessing a high boiling point than when the reactions were performed in a closed system with an aqueous solvent.31 In a previous report, however, CDs prepared from Ph in an open system using a high-boiling solvent of ethylene glycol did not show high-quality fluorescence; their PLQY was 1%.32

The emission color can be controlled by tuning the CD size due to the quantum size effect, as mentioned above.25,26 In the present study, we focused on fluorescence solvatochromism as another color-controllable strategy because we can realize different emission colors using only one size of CDs and avoid the increase in the heating duration and the use of a dehydration catalyst like H2SO4 involving additional purifications. Recently, it has been reported that the emission wavelengths of phenylenediamine-derived CDs depend on the polarities of solvents and polymers.11,30,33 This fluorescence solvatochromism is ascribed to the difference in the dipole moments in the ground state and the excited state; the emission wavelength shifts with the change in polarity of the dispersion media.35,36,37 Hence, we can readily tune the desired emission wavelength through selection of the dispersion media. However, to our knowledge, the fluorescence solvatochromism of narrow-bandwidth emissive CDs listed in Table 1 has not yet been reported.

In the present study, we successfully established a novel atmospheric glycothermal synthesis of Ph-derived CDs (Ph-CDs) whose fwhms of emission peaks were 27±40 nm. In this method, Ph was dissolved in a glycol solvent of 1,2-pentanediol possessing a boiling point of 207 °C38 and heated at 180 °C for 6 h in an open system under ambient conditions without a

Table 1. Previous Reports of Emission Peak Wavelengths (λ_em), fwhms, and Photoluminescence Quantum Yields of Narrow-Bandwidth Emissive CDs

| carbon source | synthetic method | synthetic conditions | λ_em (nm) | fwhm (nm) | PLQY (%) | refs |
|---------------|-----------------|----------------------|-----------|-----------|----------|------|
| ethylene glycol | heated in H2SO4 at 80 °C, and then stirring for 30 min after injecting deionized water | | 519 | 38 | 63 | 22 |
| formamide and glutathione | microwave solvothermal | | | | | |
| 1,4-diamino-naphthalene | solvothermal | 160 °C, 1 h | 683 | 30 | 17 | 23 |
| phloroglucinol | solvothermal | 200 °C, 12 h | 581 | 30 | 82 | 24 |
| | | 200 °C, 9 h | 472 | 30 | 66 | 25 |
| | solvothermal with HCl or H2SO4 | 200 °C, 24 h | 507 | 29 | 72 | |
| resorcinol | solvothermal | 200 °C, 2 h | 538 | 30 | 62 | |
| | | 200 °C, 5 h | 598 | 30 | 54 | |
| diaminonaphthalene and citric acid | solvothermal at 160 °C for 6 h, and then 200 °C for 1 h after adding NH4 (aq) and N2H4 hydrate for surface amination | | 433 | 35 | 70 ± 10 | 27 |
| tris(4-amino-phenyl)amine | solvothermal with tert-butyl hydroperoxide and HCl | 130 °C, 2 h | 615 ± 2 | 27 ± 1 | 84 ± 5 | 28 |
| phloroglucinol | heated in an open system | 180 °C, 6 h | 481 | 30 | 51 | this work |

Scheme 1. Schematic Illustration of the Synthetic and Color Tuning Strategy for Ph-CDs
reflux unit, as illustrated in Scheme 1. The obtained dispersion was purified by the facile and eco-friendly procedure of dialysis and centrifugation using ultrapure water to yield Ph-CD powders. We dispersed Ph-CD powders in solvents and polymers with different polarities and investigated their fluorescence solvatochromism (Scheme 1) and the feasibility of applying Ph-CDs to wide-color-gamut displays.

RESULTS AND DISCUSSION

Particulate Properties, Chemical Bonding States, and Elemental Compositions of Ph-CDs. Figure 1a shows the X-ray diffraction (XRD) profile of the Ph-CD powder. A broad diffraction peak was centered approximately 26°, which matches the peak of the (002) plane of graphite. Graphite is composed of stacked graphene layers in the c-axis orientation through π−π interactions of van der Waals forces. The lattice spacing of the (002) plane matches the spacing between the graphene layers of 0.33 nm. Numerous crystalline peaks of the Ph powder were not observed in the XRD profile of the Ph-CD powder (see Figure S1). Therefore, we concluded that the graphite structure of the obtained Ph-CDs was composed of stacked graphene in the c-axis orientation through π−π interactions.

Figure 1b depicts the Raman spectrum of the Ph-CD powder. The D band, which corresponds to the disorder and defects of the graphite structure, and the G band, which corresponds to the in-plane motion of carbon atoms, were observed at 1370 and 1590 cm⁻¹, respectively. The ordered structure of the Ph-CDs can be determined by the intensity ratio of these D and G bands (I_D/I_G). The I_D/I_G of Ph-CDs was 1.5 (Table S2), which was higher than I_D/I_G of the previously reported CDs, 1.0, indicating the high crystallinity of the graphite structure of Ph-CDs.

The transmission electron microscopy (TEM) image of Ph-CDs is shown in Figure 2. Nanoparticles of ~2 nm in size were observed in this image. As shown in Figure S2, the lattice fringes of the triangular structure with a size of approximately 1−2 nm were observed in the high-resolution TEM image. According to the fast Fourier transform (FFT) pattern (Figure S2), the spacing of the lattice fringe was evaluated to be 0.24 nm, which corresponds to the spacing of the (1120) plane of graphite.

Figure 3a illustrates the Fourier-transform infrared (FT-IR) spectrum of the Ph-CD powder. The details of the peak assignments are summarized in Figure S3 and Table S3. The peaks observed at 3100−3700, 1630, and 1158 cm⁻¹ were assigned to the stretching vibrations of O−H, C≡C, and C−O bonds, respectively. The characteristic peak at 1068 cm⁻¹ was observed in the FT-IR spectrum of the synthetic solvent of 1,2-pentanediol (Figure S3) and is assigned to the asymmetric

Figure 1. (a) XRD profile and (b) Raman spectrum of Ph-CDs.

Figure 2. TEM image of Ph-CDs.

Figure 3. (a) FT-IR and (b) C 1s XPS spectra of Ph-CDs.
stretching vibration of C−O bonds. This peak was not observed in the spectrum of the Ph-CD powder, revealing that the solvent molecule did not bind to the edge of Ph-CDs.

The peaks of C 1s and O 1s were observed in the X-ray photoelectron spectroscopy (XPS) survey scan of the Ph-CD powder (Figure S4). Figures 3b and S4 show the high-resolution scans of the C 1s and O 1s regions, respectively. The C 1s spectrum was fitted by two peaks, corresponding to C−OH (286.2 eV) and C=C bonds (284.3 eV). The peak observed at 532.5 eV in the O 1s spectrum was assigned to C−OH bonds. The presence of these bonds is consistent with the FT-IR results.

As shown in Figure S5, hydrogen signals from aromatic rings and hydroxy groups were detected at ca. 6.7 ppm and ca. 5.8 ppm in the 1H nuclear magnetic resonance (NMR) spectrum (DMSO-d6, ppm) of the Ph-CDs, respectively. The chemical shifts of the hydrogen signals from aromatic rings were noticeably different between the Ph-CDs and Ph. The signal was detected at ca. 5.6 ppm in the 1H NMR spectrum (DMSO-d6, ppm) of Ph. The difference of their chemical shifts indicates that the aromatic structure of the prepared Ph-CDs was completely different from that of Ph.

The above-mentioned results confirm that the prepared Ph-CDs contain the ordered graphite structure of the π-conjugated systems and the homogeneous surface functional groups of OH.

As illustrated in Table 2, the proportions of C−OH and C=C bonds were calculated from the areas of the fitted C 1s XPS peaks (Figures 3b and S4). The proportion of C−OH bonds in the Ph-CD powder was 21.6%, which was lower than that in the Ph powder (39.8%). The proportion of C=C bonds in the Ph-CD powder was 78.4%, which was higher than that in the Ph powder (60.2%). These results indicate that dehydration and condensation reactions between Ph molecules were facilitated in the synthetic process, implying the expansion of the π-conjugated structures, as shown in Scheme S1.

Table S4 shows the proportions of C, H, and O in the Ph-CD powder, as determined by elemental analysis. Because the amount of C is constant regardless of the promotion of the dehydration and condensation reactions between Ph molecules, we calculated the H/C and O/C molar ratios from the elemental proportions in Table S4 (see Table S5). The H/C and O/C ratios of the Ph-CDs were lower than those of Ph, indicating the progress of the dehydration and condensation reactions in the synthetic process.

Optical Properties of Ph-CDs Dispersed in Solvents with Different Polarities. Ph-CD powders were dispersed in seven kinds of solvents with different polarities, water, methanol, ethanol, benzyl alcohol, dimethyl sulfoxide (DMSO), N,N-dimethylformamide (DMF), and 1-methyl-2-pyrrolidone (MP), and these dispersions were transparent under white light, as shown in Figure 4.

This high dispersibility is attributed to the structure of the Ph-CDs, possessing a hydrophobic π-conjugated system and hydrophilic OH groups at the edge. The UV−vis spectra of the Ph-CD dispersions (Figure S6) showed a blueshift of the absorption peak with an increase in the solvent polarity. The emission color of these dispersions changed from green to blue under UV light as the solvent polarity increased, as shown in Figure 4. The peaks observed in these UV−vis, photoluminescence excitation (PLE), and PL spectra (Figures 5, S6, and S7) were assigned to the HOMO−LUMO transition [ground state (S0)−excited state (S1) transition; see Figures S8 and S9].

Table 2. Proportions of Different Bonds Calculated from Fitting of the C 1s XPS of Ph-CDs and Ph

| sample   | C−OH (%) | C=C (%) |
|----------|----------|---------|
| Ph-CDs   | 21.6     | 78.4    |
| Ph       | 39.8     | 60.2    |

Figure 4. Photographs of Ph-CD dispersions under white light and 365 nm UV light.

Figure 5. Normalized (a) PLE and (b) PL spectra of Ph-CD dispersions.
The PL peaks were extraordinarily sharp, and the fwhms of the respective PL spectra (see Table S6) were 27–40 nm. These values were narrower than those of previously reported excitation-dependent emissive CDs (≥60 nm) and comparable to those of QDs (Table S1).

The PLE and PL peaks shifted to shorter wavelengths as the solvent polarity increased. The emission energy linearly increased with the increase in each solvent polarity parameter $E_T(30)$ (Figure 6 and Table S7), which reveals the negative fluorescence solvatochromism of Ph-CD dispersions.\(^{36}\)

These results indicate that this negative fluorescence solvatochromism was attributed to the solvation effect rather than the localized effect of the formation of hydrogen bonds between the surface of the CDs and the solvent molecules. Hence, the ground state of Ph-CDs stabilized due to solvation with increasing solvent polarity because the obtained Ph-CDs had a larger dipole moment in the ground state rather than in the excited state (Figure 7).\(^{36}\)

Solvatochromism is not a common feature for phosphors. Inorganic phosphors doped with rare earth or transition metals, and semiconductor QDs do not exhibit solvatochromism. Although fluorescent organic molecules show solvatochromism, CDs do not always exhibit fluorescence solvatochromism. In fact, CDs prepared from α-glucose and L-cysteine in our previous reports did not show the solvatochromic behavior.\(^{33,34,52}\) Fluorescence solvatochromism for CDs has recently received a great deal of attention as their color tuning strategy and studied because CDs prepared from an aromatic compound of p-phenylenediamine showed the solvatochromic behavior.\(^{33,34,52}\) CDs prepared from aromatic compounds possessed π-conjugated systems, and their emission peaks shifted to longer wavelengths as the solvent polarity increased, that is, positive fluorescence solvatochromism.\(^{11,30,33,35,52,53}\) CDs prepared from nonaromatic compounds and possessing π-conjugated graphitic domains also exhibited positive fluorescence solvatochromism.\(^{34,55}\) This positive fluorescence solvatochromism is attributable to the reduction of the energy gaps of the CDs with increasing solvent polarity.\(^{30,35,36}\) In contrast, we found out that the emission peaks of the Ph-CDs shifted to shorter wavelengths as the solvent polarity increased, that is, negative fluorescence solvatochromism. Thus, the Ph-CDs exhibited opposite shifts compared to the previously reported CDs.

All the UV–vis (Figure S6) and PLE spectra (Figures 5a and S7) of the Ph-CD dispersions had shoulders and multiple peaks in the range from 350 to 550 nm and were fitted by six peaks (see Figure S8). These shoulders and peaks in the range from 400 to 550 nm were attributable to the transitions from the lowest vibrational level of the ground state ($S_0$) to several vibrational levels of the excited state ($S_1$) for the π-conjugated structure.\(^{25,49}\) The peaks on the high energy side of their spectra ranging from 350 to 400 nm were attributable to the transitions from the lowest vibrational level of the ground state ($S_0$) to several vibrational levels of the excited state ($S_1$) for the π-conjugated structure.\(^{25,49}\) All the PL spectra of the Ph-CD dispersions had shoulders and were fitted by three peaks (see Figure S9). These shoulders were attributable to the transitions from the lowest vibrational level of the excited state ($S_1$) to several vibrational levels of the ground state ($S_0$) for the π-conjugated structure (see Figure S9).\(^{25,49}\) Figure S10 shows the respective PL spectra of the Ph-CD dispersions as a function of emission energy. The respective fwhms are shown in Table S6. The fwhm increased with the increase in each solvent polarity parameter $E_T(30)$ (Figure S11). This relationship was similar to that between the solvent polarity parameter $E_T(30)$ and the emission energy (Figure 6). This indicates that the change in the fwhms can be attributed to the solvation effect. This change resulted in the change in the intensities of the shoulders of the PL spectra and their shape.

While Yuan et al. produced blue- and green-emitting CDs with fwhms of 30 and 29 nm, respectively, from Ph under high pressure using an autoclave at 200 °C by changing the heating duration from 9 to 24 h, followed by column chromatography purification using hazardous dichloromethane,\(^{25}\) we successfully produced blue- and green-emitting Ph-CDs with fwhms of 30 and 27 nm, respectively, in an open system under ambient conditions at temperatures as low as 180 °C and reaction times as short as 6 h, followed by facile and eco-friendly dialysis purifications using ultrapure water and redispersion in solvents by taking advantage of fluorescence solvatochromism. The PLQYs of both the blue and green emissions for the ethanol and DMSO dispersions of Ph-CDs were 51% (Table S6 and Figure S12). Hence, the effective preparation of Ph-CDs with multicolor narrow bandwidth emissions and high PLQYs was established. This novel type of atmospheric glycothermal method can also contribute to the mass production of narrow-bandwidth emissive CDs because this open reaction system does not depend on the volume of a container and pressure to produce the CDs compared with the closed system using an autoclave (Table 1).

---

**Figure 6.** Relationship between the solvent polarity parameter $E_T(30)$ and emission energy for Ph-CD dispersions.

**Figure 7.** Proposed schematic illustration of the change in energy gaps of the Ph-CDs in different solvents.
The PL peak wavelengths for all the dispersions of Ph-CDs kept almost constant, regardless of the excitation wavelengths (Figure S13). This result indicates that the emission of the prepared Ph-CDs is independent of the excitation wavelength, in contrast to the excitation-dependent emission of the CDs prepared through the pyrolysis and carbonization of organic molecules. This excitation-independent emission of Ph-CDs is ascribed to their ordered π-conjugated structures and homogeneous surface functional groups, as mentioned above. This agrees well with the results of PL decay curves of Ph-CD dispersions (Figure S14), which were fitted with the monoexponential equation. The PL lifetimes were evaluated to be 3.4−4.8 ns (Table S8).

As shown in the chromaticity coordinates converted from the PL spectra of the Ph-CD dispersions (Figure 8 and Table S9), these dispersions exhibited colors across the range of blue and green because of their narrow-bandwidth emissions and negative solvatochromic behavior. Notably, their color gamut exceeded the green vertex of the color system BT.709 of the conventional high-definition display and was close to that of the NTSC and the Adobe RGB.

**Optical Properties of Ph-CDs Dispersed in Different Polymers.** To investigate the feasibility of applying the prepared Ph-CDs to wide-color-gamut displays and LEDs, we formed Ph-CDs/polymer composite films using polyvinyl alcohol (PVA) and polyvinyl pyrrolidone (PVP). The Ph-CDs were uniformly distributed in each polymer film, as shown in Figure 9. These Ph-CDs/PVA and Ph-CDs/PVP films exhibited blue and green emissions, respectively, under UV light (Figure 9).

The PLE peaks of the Ph-CDs/PVA and Ph-CDs/PVP films were located at 465 and 485 nm, respectively, and their PL peaks were located at 474 and 494 nm, respectively (Figures 10 and S15), indicating that those peak positions depend on the polymers. This color change is explained by the fluorescence solvatochromism attributed to the similarity in polarity between the polymers and the dispersions. These sharp PL peaks were similar to those of the dispersions; their fwhms were 33 and 35 nm, respectively.

We attached both Ph-CDs/PVA and Ph-CDs/PVP films to a commercial UV LED to investigate the practical use of the Ph-CDs for wide-color-gamut displays and LEDs, as shown in Figure 11. These Ph-CDs/PVA and Ph-CDs/PVP films converted the UV light to blue and green emissions, respectively, under white light. These results verify that the solvatochromic color-tuning strategy can design wavelength conversion films of desired emissive colors using polymers with appropriate polarities and the obtained Ph-CDs have substantial potential for practical application in wide-color-gamut displays and LEDs.

**CONCLUSIONS**

We successfully prepared narrow-bandwidth emissive Ph-CDs at temperatures as low as 180 °C for a reaction duration of as
short as 6 h under ambient conditions without any catalysts via an open reaction system using a glycol solvent of 1,2-pentanediol. The intermolecular dehydration and condensation reactions among Ph were facilitated in the open system, resulting in the ordered graphite structure and the homogeneous surface functional groups of OH of Ph-CDs. Ph-CD powders were dispersed in seven solvents with different polarities because of the hydrophobic π-conjugated system and hydrophilic OH groups. The emission peak of Ph-CDs was readily tuned from 463 to 511 nm by taking advantage of negative fluorescence solvatochromism. They exhibited excitation-independent narrow-bandwidth blue and green emissions with respective fwhms of 30 and 27 nm and high PLQYs of up to 51%. Ph-CD polymer composite films showed a similar solvatochromic behavior and narrow-bandwidth emissions. This novel atmospheric glycothermal preparation of narrow-bandwidth emissive CDs can contribute to their use in wide-color-gamut displays and LEDs.

**EXPERIMENTAL SECTION**

**Reagents.** Ph (99%), benzyl alcohol (99.0%), MP (>99.0%), and PVP (Mw 360,000) were purchased from FUJIFILM Wako Pure Chemical Industries. 1,2-pentanediol (>98.0%) was purchased from Tokyo Chemical Industry. Methanol (99.8%), ethanol (99.5%), DMF (99.5%), and DMSO (99.0%) were purchased from Kanto Chemical Corporation. PVA (87–89% hydrolyzed, Mw 85,000–124,000) was purchased from Sigma-Aldrich. All reagents were used as received without further purification.

**Preparation of Powders and Dispersions of Ph-CDs.** Ph-CDs were prepared via an effective method through the heating in an open reaction system using a high boiling solvent. Ph (2.0 g) was added into a recovery flask (100 mL) containing the high boiling solvent of 1,2-pentanediol (40 mL) and dissolved in the solvent using ultrasonication. This solution was heated at 180 °C for 6 h with the use of an oil bath under ambient conditions and without a reflux unit. After cooling the flask to room temperature, the obtained suspension was dialyzed in ultrapure water (1 L) using a dialysis membrane (molecular weight cutoff of 3500 Da: pore size of 1 nm) for 2 days while stirring. In this dialysis, the ultrapure water was changed three times. During the purification process of this dialysis, precursors of Ph-CDs, unreacted materials, and 1,2-pentanediol molecules with the diameters less than 1 nm were removed. After adding ultrapure water (30 mL) into the dialyzed suspension (10 mL), this mixture was centrifuged at ~16,000g (13,000 rpm using a rotor with a diameter of 10 cm) for 5 min. The supernatant solution was removed to collect the precipitate. After adding ultrapure water (30 mL) into the collected precipitate, the resulting mixture was centrifuged at the same rotation speed. The supernatant solution was removed to yield the precipitate. 1,2-Pentanediol was eliminated through this centrifugation process. The collected precipitate was dried using a rotary evaporator to yield Ph-CD powder. The prepared Ph-CD powder was dispersed in water, methanol, ethanol, benzyl alcohol, DMSO, DMF, and MP to obtain the seven kinds of Ph-CD dispersions. The absorbance of each Ph-CD dispersion was adjusted to be 0.05 at its each PLE peak wavelength for analysis.

**Preparation of Ph-CDs/PVA Film.** PVA (0.50 g) was added into ultrapure water (4.5 mL), stirred for 15 min, and heated at 60 °C for 20 min under stirring. The Ph-CD powder (1.0 mg) was dispersed in ultrapure water (4 mL). This water dispersion of Ph-CDs (1 mL) was uniformly mixed with the prepared PVA aqueous solution (4.5 mL) under stirring and ultrasonication. The obtained mixture was poured into a polytetrafluoroethylene (PTFE) Petri plate (30 mmø × 12 mmH) and dried for 3 days under ambient conditions in the dark to obtain the Ph-CDs/PVA film with a Ph-CD concentration of 0.05 wt %.

**Preparation of Ph-CDs/PVP Film.** PVP (0.50 g) was dissolved in ethanol (4.5 mL) using ultrasonication. The Ph-CD powder (1.0 mg) was dispersed in ethanol (4 mL). This ethanol dispersion of Ph-CDs (1 mL) was added into the prepared PVP ethanol solution (4.5 mL) and uniformly dispersed in the solution under stirring and ultrasonication. The obtained mixture was poured into the PTFE Petri plate and dried for 1 day under ambient conditions in the dark to obtain Ph-CDs/PVP film with a Ph-CD concentration of 0.05 wt %.

**Characterization.** XRD profiles of Ph and Ph-CD powder samples were measured on an X-ray diffractometer (Rigaku, Rint-2200) with a Cu Kα radiation source and a monochromator. The Raman spectrum of the Ph-CD powder sample was recorded on a Raman microscope (Renishaw, in Via StreamLine) with a 532 nm laser. The Raman spectrum was fitted by two peaks using a software program (OriginLab Corp., Origin Pro 2019). The particle sizes and morphologies of Ph-CDs were observed with a field-emission transmission electron microscope (FEI, Tecnai G2) at 200 kV. The sample for TEM observation was prepared by drying a drop of the concentrated Ph-CD dispersion in ethanol on a copper grid covered with an ultrathin carbon-deposited film (Oken Shoji, HRC-C10) overnight. FT-IR absorption spectra of powder samples and 1,2-pentanediol in the pressed KBr disks were measured on a spectrometer (JASCO, FT/IR-4200). Chemical bonding states of powder samples were determined by XPS with an X-ray photoelectron spectroscopy instrument (JEOL, JPS-9010TR) using an Al Kα radiation source. The peak of C 1s at 284.4 eV was used for the charge-up correction. 1H NMR spectra were recorded at 500 MHz on a spectrometer (JEOL, JNM-ECAS00), and chemical shift was referenced internally to a residual DMSO signal at 2.49 ppm. The elemental composition of the Ph-CD powder was determined with an elemental analyzer (Elementar Analytical, Vario EL). The proportions of individual elements were qualified from the analysis of decomposed gas species in argon gas. UV–vis absorption spectra of Ph-CD dispersions were measured with an UV/visible/near-infrared optical absorption spectrometer.
470 nm LEDs as the light sources. These curves were fluorescence lifetime spectrometer (Hamamatsu Photonics, JASCO, FP-6500). PLE and PL spectra of Ph-CD dispersions were measured with a fluorescence lifetime spectrometer equipped with an integrating sphere (JASCO, ISF-513); the excitation light was vertically irradiated onto the front side, and the emitted light was collected by the integrating sphere on the back side for detection. The spectral response was calibrated against a solution of rhodamine B in ethylene glycol (5.5 g L\(^{-1}\)) and a standard light source (JASCO, ESC-333). The PLQY of each Ph-CD dispersion was calculated relative to 95% of rhodamine 6G in ethanol. The absolute PLQY of each Ph-CD dispersion was measured with a quantum efficiency measurement system (Otsuka Electronics, QE-2000-311C). PL decay curves of Ph-CD dispersions were recorded on a fluorescence lifetime spectrometer (Hamamatsu Photonics, Quantaurus-Tau C11367), which was equipped with 405 and 470 nm LEDs as the light sources. These curves were fitted with the following monoeponential eq 1

\[ f(t) = A \exp(-t/\tau) \]  

where \( f(t) \) is the PL intensity at time \( t \), \( A \) is the amplitude, and \( \tau \) is the PL decay time.

**ASSOCIATED CONTENT**

1) Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c05993.

Previous reports of QDs of CdSe/ZnS, CdSe/CdS/ZnS, CdSe/Cds, Cd\(_{1-x}\)Zn\(_x\)S/ZnS, InP/ZnS, cesium lead halide perovskites (CsPbX\(_3\), \( X = \text{Cl, Br, and I} \)), and organometal halide perovskites (CH\(_3\)NH\(_2\)PbX\(_3\), \( X = \text{Cl, Br, and I} \)); schematic illustration of the formation process of Ph-CDS; XRD profiles of Ph-CDS and Ph; intensities of the decomposed D (I\(_D\)) and G (I\(_G\)) and the calculated intensity ratio (I\(_G\)/I\(_D\)); high-resolution TEM image and FFT pattern of Ph-CDS; FT-IR spectra of Ph-CDS, Ph, and 1,2-pentanediol; assignment of FT-IR absorption peaks of Figure S3; XPS survey and high-resolution scans of Ph-CDS and Ph; \(^1\)H NMR spectra of Ph-CDS and Ph; proportions of C, H, and O of Ph-CDS determined by elemental analysis; elemental molar ratios of Ph-CDS and Ph determined from Table S4; UV–vis spectra of Ph-CDS dispersions; PLE and PL spectra of each Ph-CDS dispersion; schematic illustration of the S\(_0\) → S\(_1\) transitions from the ground state to the excited state including vibration levels, and the PLE spectrum of the Ph-CDS dispersion in MP and its peak fitting results; schematic illustration of the S\(_1\) → S\(_0\) transitions from the excited state to the ground state including vibration levels and the PL spectrum of the Ph-CDS dispersion in ethanol and its peak fitting results; PLE and PL peak wavelengths of Ph-CDS dispersions, fwhms of their PL spectra, and their PLQYs; solvent polarity parameter \( E_P(30) \) values and emission peak wavelengths and energies for Ph-CDS dispersions; normalized PL spectra of Ph-CDS dispersions; relationship between the solvent polarity parameter \( E_P(30) \) and fwhms of the PL spectra of Ph-CDS dispersions; spectra of each solvent and Ph-CDS dispersion for evaluating the absolute PLQY in the regions of 400–900 and 400–700 nm; PL spectra of Ph-CDS dispersions, excited by different excitation wavelengths; PL decay curves of Ph-CDS dispersions; PL decay lifetimes of Ph-CDS dispersions; chromaticity coordinates converted from the PL spectra of Ph-CDS dispersions; and PLE and PL spectra of Ph-CDS/PVA and Ph-CDS/PVP films (PDF).

**AUTHOR INFORMATION**

**Corresponding Authors**

Yoshiki Iso — Department of Applied Chemistry, Faculty of Science and Technology, Keio University, Yokohama 223-8522, Japan; orcid.org/0000-0001-7483-2828; Phone: +81 45 566 1558; Email: iso@appc.keio.ac.jp; Fax: +81 45 566 1551

Tetsuhiko Isole — Department of Applied Chemistry, Faculty of Science and Technology, Keio University, Yokohama 223-8522, Japan; orcid.org/0000-0001-8629-1002; Phone: +81 45 566 1554; Email: isobe@appc.keio.ac.jp; Fax: +81 45 566 1551

**Authors**

Taishu Yoshinaga — Department of Applied Chemistry, Faculty of Science and Technology, Keio University, Yokohama 223-8522, Japan

Momoka Shinoda — Department of Applied Chemistry, Faculty of Science and Technology, Keio University, Yokohama 223-8522, Japan

Akihiro Ogura — Department of Applied Chemistry, Faculty of Science and Technology, Keio University, Yokohama 223-8522, Japan; orcid.org/0000-0001-7483-2828

Ken-ichi Takao — Department of Applied Chemistry, Faculty of Science and Technology, Keio University, Yokohama 223-8522, Japan; orcid.org/0000-0001-8629-1002

Complete contact information is available at: https://pubs.acs.org/doi/10.1021/acsomega.0c05993

**Notes**

The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

This work was supported by the Japan Society for the Promotion of Science via KAKENHI grant number JP19K22236. T.Y. thanks the Japan Society for the Promotion of Science for the doctoral fellowship (DC2).

**REFERENCES**

(1) Xu, X.; Ray, R.; Gu, Y.; Ploehn, H. J.; Gearheart, L. J.; Raker, K.; Scrivens, W. A. Electrophoretic Analysis and Purification of Fluorescent Single-Walled Carbon Nanotube Fragments. J. Am. Chem. Soc. 2004, 126, 12736–12737.

(2) Sun, Y.-P.; Zhou, B.; Lin, Y.; Wang, W.; Fernando, K. A. S.; Pathak, P.; Mianzii, M. J.; Harruff, B. A.; Wang, X.; Wang, H.; Luo, P.; Yang, H.; Kose, M. E.; Chen, B.; Veca, L. M.; Xie, S.-Y. Quantum-Sized Carbon Dots for Bright and Colorful Photoluminescence. J. Am. Chem. Soc. 2006, 128, 7758–7759.

(3) Liu, H.; Ye, T.; Mao, C. Fluorescent Carbon Nanoparticles Derived from Candle Soot. Angew. Chem., Int. Ed. 2007, 46, 6473–6475.

(4) Baker, S. N.; Baker, G. A. Luminous Carbon Nanodots: Emergent Nanolights. Angew. Chem., Int. Ed. 2010, 49, 6726–6744.

(5) Pan, D.; Zhang, J.; Li, Z.; Wu, M. Hydrothermal Route for Cutting Graphene Sheets into Blue-Luminescent Graphene Quantum Dots. Adv. Mater. 2010, 22, 734–738.
Carbon Dots as Nanosensors for pH and Temperature. Mater. 2018, 1604436.

Controlled Graphitization and Surface Functionalization. Nature Photonics 2019, 14, 171–176.

Graphene Quantum Dots for Bioimaging, Sensor, Catalytic and Cancer Therapy and Optoelectronics. Adv. Mater. 2015, 27, 1663–1667.

ACS Omega http://pubs.acs.org/journal/acsofd
(44) Qu, D.; Sun, Z.; Zheng, M.; Li, J.; Zhang, Y.; Zhang, G.; Zhao, H.; Liu, X.; Xie, Z. Three Colors Emission from S,N Co-Doped Graphene Quantum Dots for Visible Light H₂ Production and Bioimaging. Adv. Opt. Mater. 2015, 3, 360−367.
(45) Colthup, N. B.; Daly, L. H.; Wiberley, S. E. Introduction to Infrared and Raman Spectroscopy, 3rd ed.; Elsevier: Amsterdam, 1990; pp 264, 333, 387, 392, 428.
(46) Larkin, P. J. Infrared and Raman Spectroscopy: Principles and Spectral Interpretation, 2nd ed.; Elsevier: Amsterdam, 2017; pp 118, 119, 185, 186.
(47) Wang, Z.; Yuan, F.; Li, X.; Li, Y.; Zhong, H.; Fan, L.; Yang, S. 53% Efficient Red Emissive Carbon Quantum Dots for High Color Rendering and Stable Warm White-Light-Emitting Diodes. Adv. Mater. 2017, 29, 1702910.
(48) Silverstein, R. M.; Webster, F. X.; Kiemle, D. J.; Bryce, D. L. Spectrometric Identification of Organic Compounds, 8th ed.; Wiley: Hoboken, 2014; pp 137, 147, 184, 187.
(49) Kondo, Y.; Yoshiura, K.; Kitera, S.; Nishi, H.; Oda, S.; Gotoh, H.; Sasada, Y.; Yanai, M.; Hatakeyama, T. Narrowband Deep-Blue Organic Light-Emitting Diode Featuring an Organoboron-Based Emitter. Nat. Photonics 2019, 13, 678–682.
(50) Yoshinaga, T.; Iso, Y.; Isobe, T. Particulate, Structural, and Optical Properties of D-Glucose-Derived Carbon Dots Synthesized by Microwave-Assisted Hydrothermal Treatment. ECS J. Solid State Sci. Technol. 2018, 7, R3034–R3039.
(51) Yoshinaga, T.; Iso, Y.; Isobe, T. Optimizing the Microwave-Assisted Hydrothermal Synthesis of Blue-Emitting L-Cysteine-Derived Carbon Dots. J. Lumin. 2019, 213, 6–14.
(52) Lin, S.; Lin, C.; He, M.; Yuan, R.; Zhang, Y.; Zhou, Y.; Xiang, W.; Liang, X. Solvatochromism of Bright Carbon Dots with Tunable Long-Wavelength Emission from Green to Red and Their Application as Solid-State Materials for Warm WLEDs. RSC Adv. 2017, 7, 41552–41560.
(53) Lee, H. J.; Jana, J.; Ngo, Y.-L. T.; Wang, L. L.; Chung, J. S.; Hur, S. H. The Effect of Solvent Polarity on Emission Properties of Carbon Dots and Their Uses in Chlorimetric Sensors for Water and Humidity. Mater. Res. Bull. 2019, 119, 110564.
(54) Pramanik, A.; Biswas, S.; Kumbhakar, P. Solvatochromism in Highly Luminescent Environmental Friendly Carbon Quantum Dots for Sensing Applications: Conversion of Bio-Waste. Spectrochim. Acta, Part A 2018, 191, 498−512.
(55) Basu, N.; Mandal, D. Solvatochromic Response of Carbon Dots: Evidence of Solvent Interaction with Different Types of Emission Centers. J. Phys. Chem. C 2018, 122, 18732–18741.
(56) Yang, L.; Jiang, W.; Qiu, L.; Jiang, X.; Zuo, D.; Wang, D.; Yang, L. One Pot Synthesis of Highly Luminescent Polyethylene Glycol Anchored Carbon Dots Functionalized with a Nuclear Localization Signal Peptide for Cell Nucleus Imaging. Nanoscale 2015, 7, 6104–6113.
(57) Zhu, S.; Song, Y.; Zhao, X.; Shao, J.; Zhang, J.; Yang, B. The Photoluminescence Mechanism in Carbon Dots (Graphene Quantum Dots, Carbon Nanodots, and Polymer Dots): Current State and Future Perspective. Nano Res. 2015, 8, 355–381.