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Studying the Optical Transitions of Carbon Dots from o-Phenylenediamine Depending on the Solvents and Additional Precursors

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In recent years, carbon dots have attracted much scientific attention due to their unique properties, which can find applications in many fields. We have developed synthesis protocols of carbon dots with different structure and optical properties using o-phenylenediamine. The change in absorption and luminescence spectra of carbon dots were studied in detail. The obtained samples show intensive luminescence at 350 nm and 450 or 550 nm dependent on synthesis parameters.

Keywords: Carbon dots, photoluminescence, spectroscopy.

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Introduction

Carbon is known as the material that is incapable of emitting light, but carbon dots (CDs) have attracted the attention of numerous research groups around the world because of their intense emission, whose spectral position can be tuned. The core of CDs is composed from sp^2-/sp^3-hybridized carbon atoms with different functional groups on the surface [1]. This nanomaterial has such advantages as water solubility, biocompatibility, photostability, low precursor cost and cytotoxicity, high sensitivity to external environment compared to conventional luminescent nanoparticles [2]. This combination of properties allows the use of CDs in a wide range of applications from optoelectronics and sensing to biovisualization.

A unique feature of CDs is the tunable photoluminescence (PL) band from the deep ultraviolet (UV) to near-infrared (NIR) spectral range. The optical properties of CDs depend on their structure, size, shape, and chemical composition. These characteristics can be controlled during synthesis by using different precursors and solvents, as well as by changing physical parameters such as temperature and reaction time. In the synthesis process, luminescent centers are formed, which can be located both inside the core of the CDs and on their surface. [3,4].

In this work, CDs samples were synthesized by the solvothermal method. O-phenylenediamine (o-pd) was used as the main precursor. The optical transitions and their intensity can be controlled by adding additional precursors and changing the solvent. Moreover, the use of benzoic acid as a precursor produces emission in the blue spectrum area, excited by longer wavelength radiation (600−650 nm). Thus, the developed CDs are of great interest for applications such as bio-visualization and sensing.

Materials and research techniques

CDs synthesis

Seven samples of CDs were synthesized by the solvothermal method described in [5]. Additional precursors, their masses, and solvents are presented in Table 1. Benzoic acid and thiourea were selected as additional precursors. Briefly, 6 g o-pd with or without additional precursor was dissolved in 25 mL of solvent. The solutions were placed in a Teflon–lined autoclave and heated at 180°C for 6 h. The obtained solutions were purified from large particles and agglomerates through a filter with a $0.22\,\mu$m membrane and dialyzed with dialysis tube with 2 kDa molecular weight cut-off against deionized water for 1 day. To measure the optical properties, the samples were dissolved in water.

O-phenilenediamine (99.5%), benzoic acid ($\geq 99.5\%$), thiourea ($> 99\%$), hydrochloric acid (HCl) ($\geq 95\%$), ethanol ($> 96\%$) were purchased from Vekton. Water was purified using the milli-Q water purification system ($18.2\,\mathrm{M\Omega}$) from Millipore.

Research methods

Absorption spectra were measured using a UV-3600 spectrophotometer (Shimadzu). PL excitation-emission (PLE-PL) maps of the samples were obtained on a spectrofluorometer FP-8200 (Jasco). Fourier transform infrared (FTIR) spectra were obtained on a infrared spectrophotometer Tenzor II (Bruker). The PL decay curves were obtained using a laser scanning microscope MicroTime 100 (PicoQuant). Average PL lifetime was calculated using the

Table 1. CDs synthesis parameters: sample name, additional precursors and their masses, solvent

Sample	Additional precursor	Mass, g	Solvent
CD-1	–	–	Water
CD-2	–	–	Water+500 uL HCl
CD-3	–	–	Ethanol
CD-4	Benzoic acid	0.56	Water
CD-5	Benzoic acid	0.56	Ethanol
CD-6	Thiourea	0.7	Water
CD-7	Thiourea	0.7	Ethanol

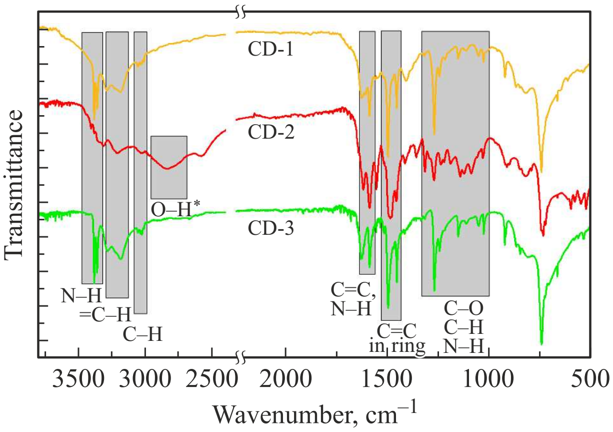

Figure 1. FTIR spectra of CD-1 (orange line), CD-2 (red line), and CD-3 (green line). Typical frequencies are shown in gray rectangles with the designation of each group type.

formula

$$\tau_{\text{av}} = \sum_i A_i\tau_i^2 \Big/ \sum_i A_i\tau_i, \tag{1}$$

where A_i and τ_i — amplitude and decay time of the ith component, respectively. The PL quantum yield (PL QY) was determined by comparing it to Rhodamine 6G using the formula

$$\varphi_{\text{CD}} = \frac{(1-10^{-D_{\text{Rh}}})S_{\text{CD}}n_{\text{CD}}^2}{(1-10^{-D_{\text{CD}}})S_{\text{Rh}}n_{\text{Rh}}^2}\varphi_{\text{Rh}}, \tag{2}$$

where D_{CD} and D_{Rh} — the optical density of CDs and Rhodamine 6G at the excitation wavelength λ, respectively; S_{CD} and S_{Rh} — the integral PL intensity of sample and dye under excitation at the wavelength λ, respectively; n_{CD} and n_{Rh} — the refractive index of the solvents in which the CDs and Rhodamine 6G are dissolved, respectively.

Results and discussion

In this work, o-pd was used as the main precursor for the synthesis of CDs. CD-1 and CD-3 were synthesized from o-pd in water and ethanol, respectively. In addition, CDs synthesis in acid medium (CD-2) was carried out which, according to the literature [6], can lead to red-shift of the PL peak. Two additional precursors were selected for surface modification: benzoic acid (CD-4, CD-5), which is a source of aromatic rings and –OH groups, and thiourea (CD-6, CD-7), which is a source of amine groups and sulfur atoms. Syntheses with these precursors were performed in water and ethanol to study the effect of the solvent on the morphology and optical properties of the obtained CDs.

CDs from o-pd synthesized in different chemical environments

The morphology of CD-1, CD-2, and CD-3 samples was examined by FTIR spectroscopy (Fig. 1). CD-1 and CD-3 have peaks at 3385 and 3365 cm^{-1} corresponding to symmetric and asymmetric vibrations of the groups –NH in primary amines. The FTIR spectrum of CD-2 contains only a weak peak at 3385 cm^{-1}, which is a consequence of the use of acid during synthesis. All samples have a broad peak in the 3000–3400 cm^{-1} region related to O–H bonds. Stretching vibration of the =C–H group at 3030 cm^{-1} are also observed and attributed to greater degree of carbonization and aromatization of the synthesized CDs [7]. For sample CD-2, absorption peak at 2840 cm^{-1} appears, which can be attributed to the stretching vibrations of the O–H group in carboxylic acids. C=H vibrations in the FTIR spectra of CD-1, CD-2 and CD-3 samples. C=C vibrations and N–H bending in aromatic amines at 1600 and 1620 cm^{-1} are present in the FTIR spectra of both samples. An intense peak of C=C-group vibrations in the aromatic ring is observed at 1500 cm^{-1}. In 1400–1200 cm^{-1} region, both bending and rocking vibrations of the C–H group, and stretching vibrations of C–O group are observed. The peak at 1560 and 1460 cm^{-1} refer to the presence of stretching vibrations of C–N groups in the aromatic ring. Thus, the surface of CD-1, CD-2 and CD-3 samples contain such groups as –CH, –OH, and –NH$_2$, with amino groups being more pronounced in CD-1 and CD-3, and OH in carboxylic group — in CD-2.

The absorption spectra and PLE-PL maps of the CD-1–CD-3 are shown in Fig. 2. All samples have an intense absorption peak at a wavelength of 260 nm, which is attributed to $\pi \rightarrow \pi^*$-transitions in the CDs core. For CD-1 and CD-3, there is a broad absorption band in the range 400–500 nm with several narrow peaks that refer to the absorption of molecular compounds with aromatic subsystem. Such peaks are typical for CDs synthesized from o-pd [5,8,9]. However, sample CD-3 has a broad peak at 420 nm with the shoulder in the region 500–570 nm.

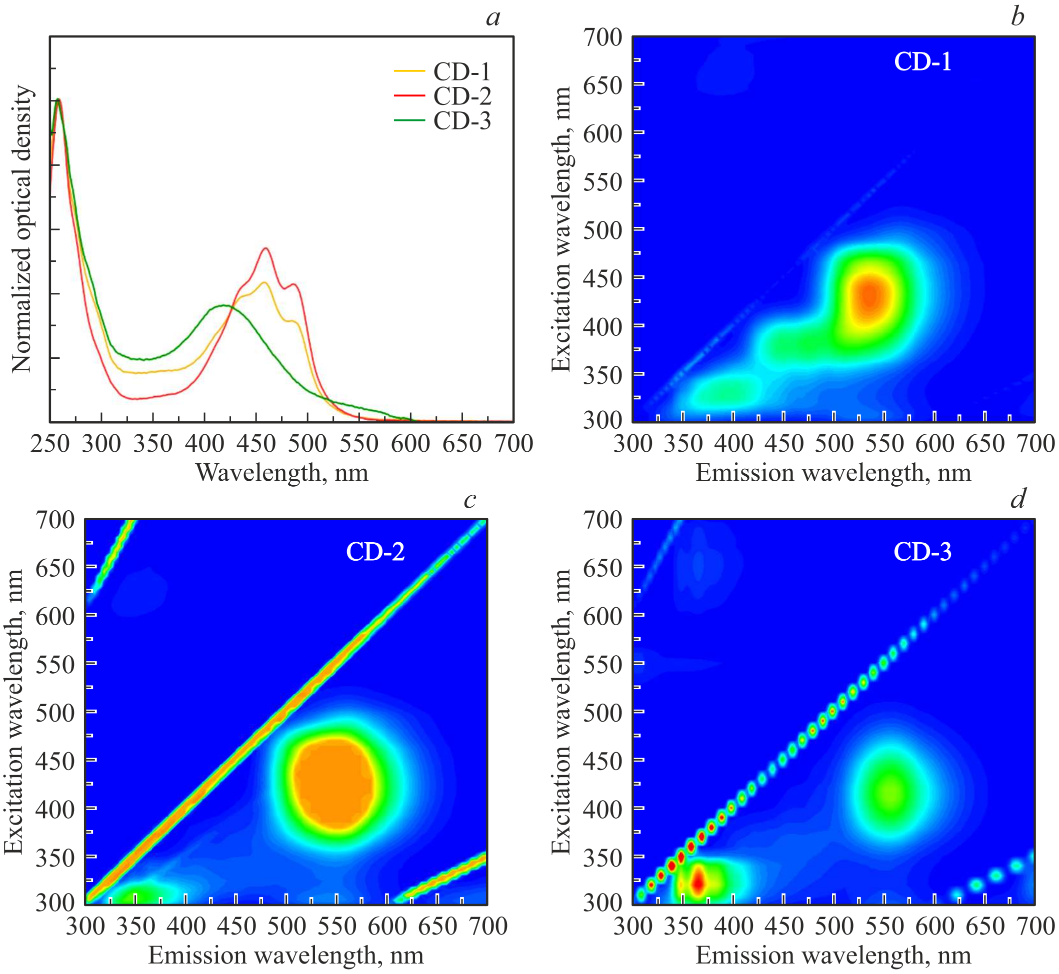

Figure 2. Optical properties of CDs samples synthesized in different chemical environments: (*a*) absorption spectra of CD-1 (orange line), CD-2 (red line) and CD-3 (green line); (*b*)–(*d*) PLE-PL maps of CD-1 (*b*), CD-2 (*c*), and CD-3 (*d*).

From PLE-PL maps (Fig. 2, *b*–*d*), it can be observed that CD-1 has three PL bands: at 360–420 nm excited at 320 nm, 420–500 nm excited at 370 nm and a broad band centered at 530 nm excited at 370–480 nm. As expected, CD-2 demonstrates a redshifted and more intensive longer-wavelength PL band centered at 550 nm compared to that of CD-1. In contrast, PL band of CD-2 sample excited by UV light blueshifts to 330–380 nm compared to PL at 360–440 nm observed for CD-1. For sample CD-3, two PL bands can be distinguished: more intense in the 340–420 nm region excited at 320 nm and less intense in the 530–560 nm region excited at 420 nm. From the absorption spectra and PLE-PL maps, we can conclude that the main intense emission in the 530–560 nm region comes from molecular compounds, including derivatives of o-pd. It is worth noticing that only for the sample synthesized in water (CD-1), there is an emission band around 450 nm, which is efficiently excited at a wavelength of 370 nm.

The PL lifetimes (τ_{av}), from biexponential approximation and the PL QY measured at 400 nm excitation wavelength, for samples CD-1, CD-2 and CD-3 are given in Table 2. Acid addition during synthesis (CD-3) did not affect either the PL lifetime or the PL QY. For CD-3 sample, the PL lifetime changed within the accuracy of the measurements, but the choice of ethanol as a solvent led to a sharp increase in the PL QY to 38%.

Thus, the addition of acid leads to a slight shift of the optical transitions, and the solvent replacement from water to ethanol leads to the blueshift and blurring the vibrational structure of absorption band together with an increase of PL QY.

CDs synthesized with benzoic acid

Fig. 3 shows FTIR spectra of CDs synthesized with benzoic acid in water (CD-4) or ethanol (CD-5). These samples also contain peaks corresponding to the C–N, C–H, C–O, C=C, and C–C groups observed in CD-1. The presence of secondary amines on the surface of the CDs was confirmed by the presence of peaks at 3430 and 3340 cm^{-1}. The addition of benzoic acid during the synthesis resulted in a broad peak at 2590 cm^{-1} related to O–H groups in

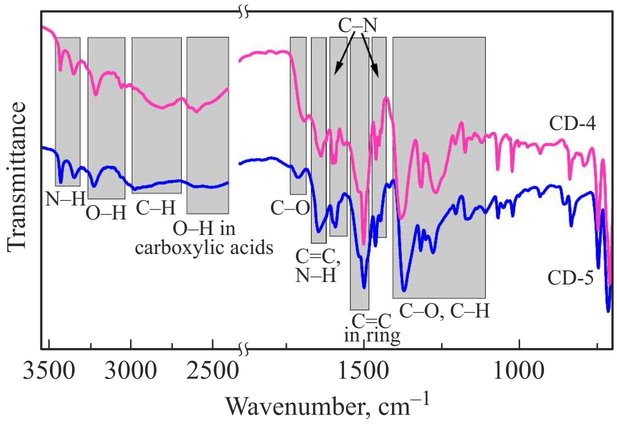

Figure 3. FTIR spectra of samples CD-4 (pink line) and CD-5 (blue line). Typical oscillation frequencies are shown in gray rectangles with the designation of each group type.

carboxylic acids, and C=O groups at 1690 cm^{-1} for CD-4 and 1710 cm^{-1} for CD-5.

The absorption spectra of CD-4 and CD-5 are shown in Fig. 4. Both samples have an absorption peak at 260 nm, as observed for CD-1. Compared with the vibrational structure in the low-energy absorption band for CD-1, samples CD-4 and CD-5 show one broad peak at 440 and 435 nm, respectively.

From PLE-PL maps, the most intense band is observed in the 350–360 nm region excited at 300 nm (Fig. 4 *b, c*). CD-4 has an excitation band at 350 nm similar to CD-1, but this peak disappears for the CD-5 sample. It should be noted that CD-5 has a more intense long-wavelength PL band than CD-4. Both samples of CDs with benzoic acid have a low-intensity anti-Stokes PL band: for CD-4, excited at 610 nm, emission around 350 nm is observed (Fig. 4,*b*); for CD-5, emission center is observed at 360 nm while excited at 630 nm (Fig. 4, *c*). This feature of the samples is attractive for biomedical applications.

Table 2. Average PL lifetime and PL QY of CD-1, CD-2, and CD-3

Sample	τ_{av}, ns	PL QY, %
CD-1	2.3 ± 0.3	4
CD-2	2.2 ± 0.3	4
CD-3	1.9 ± 0.3	38

Table 3. Average PL lifetime and PL QY of CD-4, and CD-5

Sample	τ_{av}, ns	PL QY, %
CD-4	1.8 ± 0.3	2.3
CD-5	1.7 ± 0.3	2.5

Table 3 shows the PL lifetime estimated from fitting by a biexponential function and the PL QY (excitation wavelength 400 nm) of samples CD-4 and CD-5.

Samples synthesized with benzoic acid as an additional precursor are characterized by similar average PL lifetime and PL QY to the CD-1 sample. In corresponding to this, we can assume that benzoic acid does not affect the charge relaxation in the CDs synthesized from o-phenylenediamine but results in the intensity redistribution between the emissive centers.

C-dot synthesized with thiourea

FTIR spectra of CDs synthesized with thiourea in water (CD-6) and ethanol (CD-7) are shown in Fig. 5. Unlike CD-1 , CD-6 only has a peak at 3340 cm^{-1} in the region related to N–H vibrations, and CD-7 has a shoulder in the 3440–3300 cm^{-1} region. The intense peak at 2050 cm^{-1} and the broad peak at 2570 cm^{-1} observed in the FTIR spectra of samples CD-6 and CD-7 attributed to the S–H and N=C=S groups, respectively. In comparison with CD-

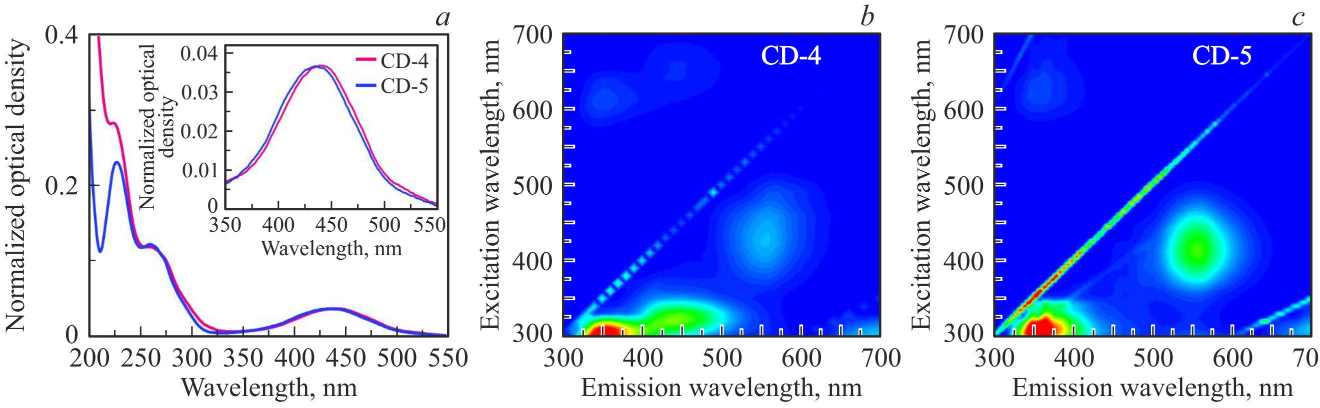

Figure 4. Optical properties of CDs with benzoic acid: (*a*) absorption spectra of CD-4 (pink line) and CD-5 (blue line); (*b, c*) PLE-PL maps of CD-4 (*b*) and CD-5 (*c*).

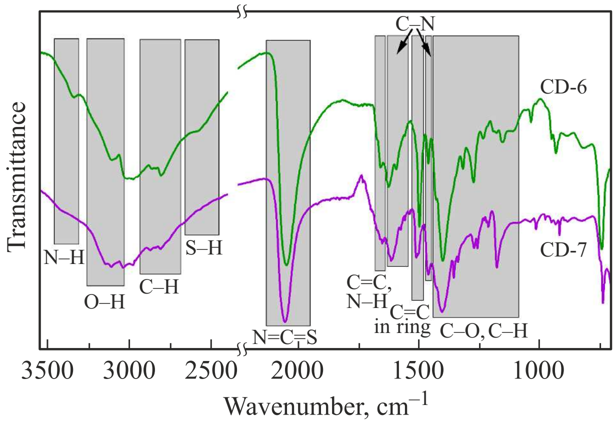

Figure 5. FTIR spectra of samples CD-6 (green line) and CD-7 (purple line). Typical oscillation frequencies are shown in gray rectangles with the designation of each group type.

6, the peak attributed to the S–H group disappears for sample CD-7.

The absorption spectra of samples with thiourea are shown in Fig. 6, *a*. As was observed for samples synthesized with benzoic acid, a single broad peak at 440 nm is observed for CD-6 and CD-7. A distinctive feature of CD-7 is the additional absorption peak at 360 nm.

It can be seen from PLE-PL maps that the CD-6 and CD-7 emission is very different (Fig. 6, *b*, *c*). For CD-6, the main PL band is in the region 500–580 nm under excitation at 400–430 nm. It should be noted that both samples CD-6 and CD-7 have a PL band excited at 360 nm, as observed in CD-1 and CD-4.

The estimated average PL lifetime and PL QY samples CD-6 and CD-7 are presented in Table 4. For CDs with thiourea, an increase in PL QY of more than two fold compared to the CD-1 sample is observed. Sample CD-7 has the longest PL lifetime among all samples.

Comparing CD-6 and CD-1 samples, we observe a decrease in the number of non-radiative transitions when thiourea is used in the synthesis, as the PL QY increases almost twice, while the lifetime of the PL remains unchanged.

Table 4. Average PL lifetime and PL QY of CD-6, and CD-7

Sample	τ_{av}, ns	PL QY, %
CD-6	1.8 ± 0.3	6
CD-7	2.5 ± 0.3	6.6

Conclusion

In this work, we developed protocols for the synthesis of carbon dots based on o-pd. The effect of synthesis parameters, such as the chemical environment and the type of additional precursor, on the optical and structural properties of CDs was investigated in detail. All CDs samples contain –CH, –OH, and –NH$_2$ groups on the surface, and the core contains aromatic compounds. The use of benzoic acid and thiourea leads to the formation of carboxylic and sulfur-containing groups on the surface, respectively. All samples have an intense absorption band at 260 nm, corresponding to $\pi \rightarrow \pi^*$ optical transitions, as well as a broad long-wavelength band, whose position and shape can be tuned by varying the chemical composition of precursors and media during CDs synthesis. The emission of all samples is observed in the range from 300 to 600 nm and can be tuned by changing the synthesis parameters. Changing the chemical medium, solvent and adding another precursor lead to an increase in the PL QY: when thiourea is added, the PL QY doubles (6.6% for CD-7), and when the solvent is changed from water to ethanol, the PL QY reaches 38% (CD-3). Moreover, CDs synthesized with benzoic acid possess anti-Stokes PL at 375 nm under excitation at 650 nm. The origin of this photo-physical process requires additional research. Thus, we demonstrated that by varying the synthesis parameters, one can obtain a set of CDs with tunable

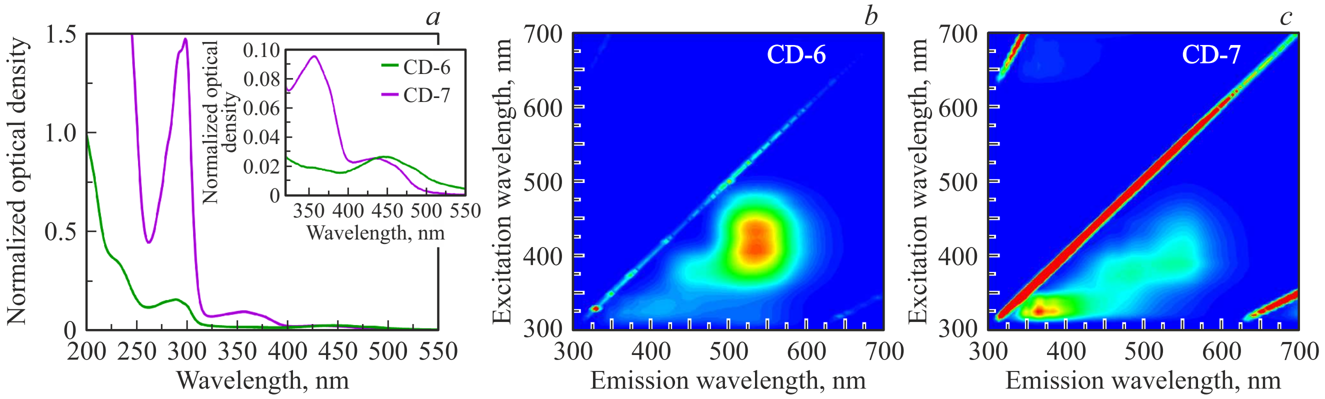

Figure 6. Optical properties of CDs with thiourea: (*a*) absorption spectra of CD-6 (green line) and CD-7 (purple line); (*b*, *c*) PLE-PL maps of CD-6 (*b*) and CD-7 (*c*) samples.

optical properties in a wide spectral range, which is very important for the use of this nanomaterial as luminescent nanoparticles in many applications, including biological ones.

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Conflict of interest

The authors declare that they have no conflict of interest.

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