Optics and Spectroscopy, 2024, Vol. 132, No. 3

20

Effect of solvent acidity and basicity on optical properties of carbon dots

© A.A. Korepanova[1], K.A. Laptinskiy[1,2], T.A. Dolenko[1,2]

[1] Department of Physics, Moscow State University,
119991 Moscow, Russia
[2] Skobeltsyn Institute of Nuclear Physics, Moscow State University,
119991 Moscow, Russia
e-mail: korepanova.aa20@physics.msu.ru

Received December 01, 2023
Revised January 11, 2024
Accepted March 05, 2024

This paper presents the study of the influence of molecules of six solvents with different acidity and basicity on the optical properties of carbon dots. Analysis of the obtained IR absorption spectra, optical density spectra and photoluminescence spectra of carbon dots in solvents showed a significant dependence of the quantum yield of photoluminescence and the energy of vibrational transitions of the surface groups of carbon dots on the acidity of the solvent. The obtained results are explained by the strengthening of hydrogen bonds between fluorophores and solvent molecules with the increase of acidity.

Keywords: Carbon dots, absorption spectroscopy, photoluminescence, acidity, basicity, quantum yield of photoluminescence, chemical equilibrium constant.

DOI: 10.61011/EOS.2024.03.58744.23-24

Introduction

The development of techniques for molecular diagnostics of various biological and processing media is highly relevant at present to several branches of science, biomedicine, and industry. In view of this, the research into construction and refinement of sensors (optical ones included) for the determination of different physical and chemical parameters of the ambient medium has picked up momentum. Carbon dots (CDs) are one of the most promising types of nanoparticles for nanosensorics, since they offer stable and intense photoluminescence (PL) in the visible range, have the capacity for surface modification, and easily synthesized from a variety of precursors [1,2]. CD-based optical sensors operate based on the variation of spectral characteristics of nanoparticle luminescence (e.g., PL intensity, position of the maximum, half-width of PL bands, etc.) upon interaction with the examined substance or upon a change in ambient parameters [3–6]. This sensitivity of PL is the reason why CDs are used widely as optical environmental sensors [3–5]. The authors of [4] have designed a CD-based photoluminescent nanosensor for simultaneous determination of concentrations of Cu^{2+}, Ni^{2+}, and Cr^{3+} metal cations and NO_3^- anions in multicomponent aqueous media. The potential for variation of adsorption and hydrophilic/hydrophobic surface properties makes CDs applicable for the purpose of extraction of toxic compounds from technical and biological liquids. Sol-gel fabrication of a nanocomposite hydrogel based on quantum CDs has been reported in [5]. Its photoluminescence is quenched by Fe^{3+} ions, and the material itself features a high adsorption index of 31.94 mg/g. These properties make the obtained nanocomposite efficient in removal of iron admixtures [5].

A combination of such properties as nontoxicity, biocompatibility, and intense and stable PL (the average quantum yield of photoluminescence is several tens of percent) make CDs suitable for application as biomarkers and for biomedical procedures involving diagnostics of the composition and state of biological tissues, determination of pH of biological media, and targeted drug delivery [2–4,6]. Specifically, the authors of [6] have proposed to use solvothermal CDs with a modified surface and complexed with 2-(2'-hydroxyphenyl)benzothiazole as a biomarker for visualization of shrinkage of cancerous tumors in the course of treatment: PL of these CDs is sensitive to viscosity, and oncological diseases are known to induce a change in viscosity of affected organs. Fast response rate, capacity for local (within volumes on the order of tens or hundreds of nm^3) monitoring of the state of a biological sample, rapid sample preparation, low cost, and ease of CD synthesis are among the advantages of these nanosensors.

Although extensive research articles and various proposals regarding the application of CDs in different branches of science and industries have already been published, studies into the mechanisms of CD PL are far from being complete: a consensus on the nature of photoluminescence of CDs has not been reached. According to literature data, both the carbon core and various functional groups on the surface of CDs may serve as sources of CD photoluminescence [7,8]. However, it is evident that efficient CD application is quite impossible if the mechanisms of emergence and variation of their photoluminescence in interaction with the environment remain obscure. Therefore, the examination of influence of various media (solvents included) parameters on the spectral characteristics of CD PL is an important stage of research into the nature of PL of nanoparticles.

Several research groups have demonstrated that the influence of a solvent on the optical properties of CDs (shape and position of absorption bands and intensity and quantum yield of photoluminescence) is quite significant [3,9–11]. Specifically, the authors of [9] have examined CDs synthesized hydrothermally from ninhydrin and o-phenylenediamine in four different solvents: water, ethanol, acetic acid, and dimethylformamide (DMF). As the concentration of CDs in solutions increased, the redshift of the PL maximum became more pronounced, while the PL intensity decreased (for all four solvents). The authors have determined that this result is attributable to the intensification of dipole-dipole energy transfer between CDs, which leads to quenching of PL of donor chromophores and excitation of PL of acceptor chromophores at longer wavelengths. Study [10] was focused on the mechanisms of variation of the quantum yield of CD PL in solution upon a change in polarity and the sum of acidity and basicity (SA+SB) of a solvent subjected to prolonged irradiation. The obtained data revealed that the quantum yield of PL decreases under the influence of excitation radiation in most examined solvents. The authors have concluded that this effect is attributable to the weakening of specific interactions of chromophores with solvent molecules under the influence of electromagnetic radiation. The authors of [11] have studied CDs produced via solvothermal synthesis from nitrilotriacetic acid and para-phenylenediamine in solvents with different polarities: water, methanol, ethanol, ethyl acetate, acetonitrile, and DMF. It was found that the photoluminescence maximum shifts toward longer wavelengths as the solvent polarity increases; alongside with that, the half-width of the PL band increases monotonically, while the quantum yield of CD luminescence decreases. The observed effects may be attributed, first, to the probable increase in carrier density driven by nitrogen-containing surface functional groups of CDs in the presence of high-polarity solvents and, second, to the fact that the energy required to alter the direction of a solvent dipole molecule increases with increasing solvent polarity. Thus, excited electrons in a high-polarity solvent lose more energy than those in a low-polarity one, and this induces a redshift of the PL maximum.

In the present study, we examine the spectral characteristics of photoluminescence of CDs, which were synthesized hydrothermally from citric acid and ethylenediamine, in solvents with different acidity and basicity parameters.

Materials and methods

Synthesis of CDs and preparation of samples

Carbon dots synthesized hydrothermally from citric acid and ethylenediamine (in a 1:1 ratio) within 3 h at a temperature of 120°C are studied. The process of synthesis and characterization of CDs was detailed in [8].

According to dynamic light scattering data, the size of CDs in water is 17.3 nm [8]. X-ray photoelectron spectroscopy revealed that just over 2/3 of all atoms in synthesized CDs are carbon (C) ones. The remaining one third of atoms is divided, in a roughly equal proportion, between oxygen (O) and nitrogen (N) atoms. IR absorption spectroscopy demonstrated that carboxyl $-COOH$, hydroxyl $-OH$, amide $-NH_2$, and nitro (NO_2) groups are present on the surface of nanoparticles [8].

Parameters of solvents used

Solvent	SB	SA
Water	0.025	1.062
Methanol	0.545	0.605
Ethanol	0.658	0.400
Isopropanol	0.830	0.283
DMSO	0.647	0.072
Acetone	0.475	0

The following solvents were used to prepare CD solutions: deionized water (a Millipore Simplicity UV water purification system was applied), ethanol, methanol, isopropyl alcohol, acetone, and dimethyl sulfoxide (DMSO). AR grade (or higher-purity) chemical reagents were used in the study. Solvents were chosen in such a way that their parameters characterizing acidic and basic properties differed significantly (see the table). Empirical Catalan [12] values of these parameters were used. The SA value characterizes donor properties of solvent molecules, while SB characterizes their acceptor properties.

Experimental methods

Prepared solutions with equal concentrations of CDs (94 mg/l) were examined using IR absorption spectroscopy, optical absorption spectroscopy, and photoluminescence spectroscopy.

IR absorption spectra were recorded with a Bruker Invenio R Fourier spectrometer, which was fitted with an ATR accessory with a diamond element, in the $400-4000\,\mathrm{cm}^{-1}$ range with a resolution of $4\,\mathrm{cm}^{-1}$.

Optical density spectra of CD solutions were measured with a dual-channel Shimadzu UV-1800 spectrophotometer in the 190−1100 nm range with a step of 1 nm at an average scanning rate. A quartz cell with a solvent was placed in the reference channel; the optical path length was 1 cm.

PL spectra of CD solutions were recorded with a Shimadzu RF-6000 spectrofluorimeter under excitation in the 200–450 nm wavelength range. PL emission spectra were measured in the wavelength range from 350 to 750 nm with a step of 1 nm at a scanning rate of 12000 nm/min and low sensitivity. This excitation wavelength was chosen for the fact that it corresponded to the maximum CD photoluminescence intensity. Samples were introduced into quartz cells with an optical path length of 1 cm.

Spectra processing consisted in normalization of optical absorption spectra to the highest absorption in the band with

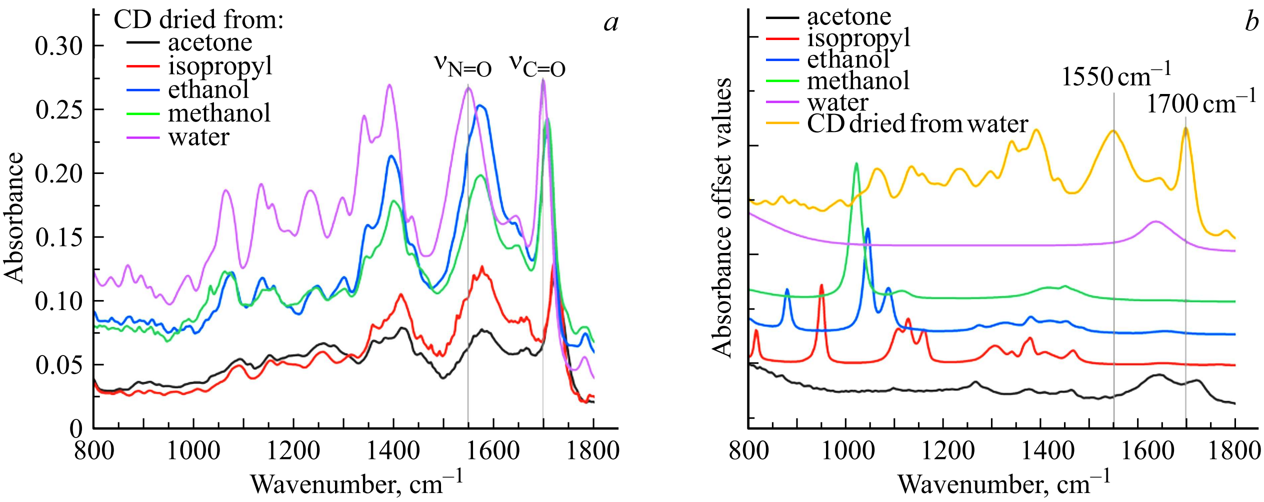

Figure 1. (*a*) IR absorption spectra of CD powders dried from different solvents. (*b*) IR absorption spectra of solvents and CDs dried from water.

its maximum around 350 nm. The Spectragryph package was used for processing.

Results and discussion

IR absorption spectroscopy

IR absorption spectra of CD powders dried from different solvents and of these solvents themselves were recorded in order to examine the effect of solvents on the structural and surface properties of CDs. CD powders from DMSO were not studied, since the solvent could not be evaporated completely. Figure 1, *b* presents the IR absorption spectra of each solvent and CDs dried from water, while Fig. 1, *a* shows the IR absorption spectra of CDs dried from all solvents.

A comparison of IR absorption spectra of a solvent and CDs dried from it (Figs. 1, *a*, *b*) reveals that solvent molecules adsorbed on the surface of nanoparticles produce a significant contribution to the IR absorption spectrum of dried CDs in the region from 1000 to 1500 cm^{-1}. Therefore, the primary focus was on the region from 1500 to 1900 cm^{-1} where the bands of surface CD groups are concentrated (this is verified by the IR absorption spectrum of CDs dried from water in Fig. 1, *b*).

It can be seen from Fig. 1, *a* that the influence of a solvent is the most pronounced for surface carboxyl and nitro groups: the position of absorption bands produced by valence vibrations of N=O and C=O bonds (maxima at 1572 and 1706 cm^{-1}, respectively [13]) varies with the solvent type. As the solvent acidity (SA parameter) increases, the maxima of the indicated bands of both carboxyl and nitro functional groups shift toward smaller wavenumbers (Fig. 2). Acidity SA characterizes the capacity of a substance to give up charge (this includes being a donor for the formation of hydrogen bonds [12]). An atom accepting a proton is called an acidity center. Protonation of the acceptor atom is the result of attachment of a proton to an acidity center [14]. Carboxyl and nitro groups rank among the acidity centers of CDs. These functional groups are characterized by a high degree of polarity, which enables the formation of strong hydrogen bonds with surrounding molecules. The observed shift of IR absorption bands is attributable to the fact that the intensity of protonation of surface CD groups by solvent molecules increases with an increase in SA, inducing a reduction in the energy of N=O and C=O vibrational transitions [15].

Optical absorption spectroscopy

Optical absorption spectra of solutions of CDs in all the used solvents were recorded in order to examine the influence of solvents on the optical properties of CDs. These spectra were normalized to the maximum of the absorption band positioned at approximately 350 nm. The primary absorption bands of CDs with maxima in the region of 245 and 350 nm, which correspond to different electronic transitions of the excited state [16,17], are indicated in Fig. 3.

It follows from the obtained data that the characteristics of both bands depend on the solvent type (Fig. 3). The band with its maximum close to 350 nm shifts significantly depending on the solvent, indicating that the electronic environment of the chromophore changes considerably [18]. The greatest difference between the positions of maxima of this absorption band (approximately $\Delta\lambda = 25$ nm) corresponds to the spectra of CDs in water and isopropanol (and in water and acetone). The observed largest shift of the band with its maximum at 350 nm correlates with the greatest difference between the acidity and basicity of the indicated solvents: water is characterized by the lowest basicity SB and the highest acidity SA, isopropanol has the highest basicity, and acetone has the lowest acidity (see the table). The

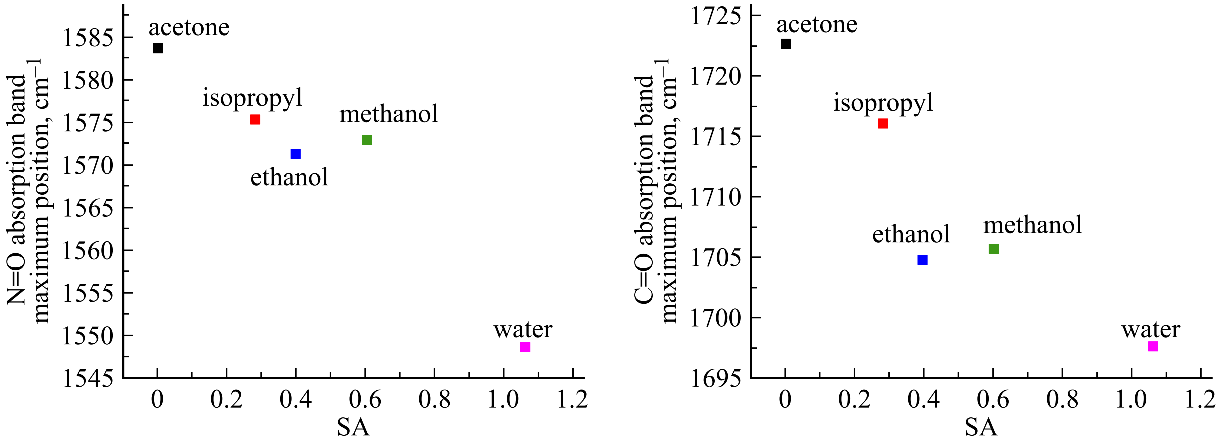

Figure 2. Dependences of the position of maxima of absorption bands of N=O and C=O bonds on solvent acidity SA.

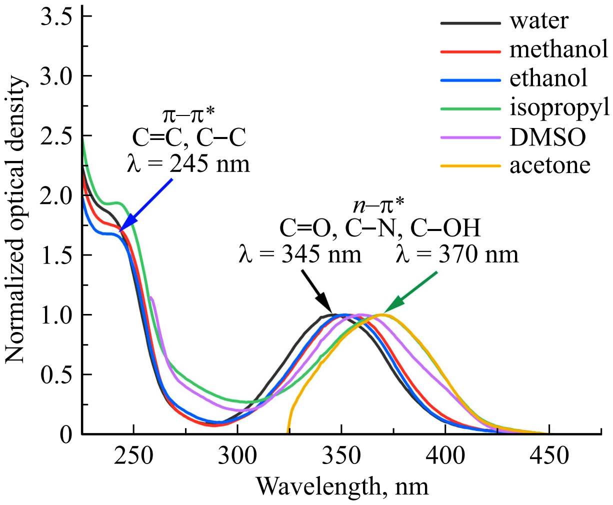

Figure 3. Optical absorption spectra of CDs in different solvents.

obtained correlation made it clear that the study of variation of optical characteristics of CDs in water, isopropanol, and acetone should yield the most meaningful and intriguing results, since these solvents exert the greatest influence on the optical density spectra of CD suspensions. It was decided to examine the optical absorption bands with their maximum around 350 nm of CDs in binary isopropanol-water and acetone-water solutions with the concentration of water varying from the highest possible value of 100% to 0.5% (Fig. 4).

It can be seen from Fig. 4, *a* that the optical density at a wavelength of 350 nm for CDs in a binary isopropanol-water solution remains constant as the water concentration varies from 100 to 25%. A similar effect is observed in the other binary solution (Fig. 4, *b*): at a wavelength of 350 nm, the optical density remains constant as the water concentration varies from 100 to 62.5%. Thus. the examined absorption bands have an isosbestic point at a wavelength of $\lambda = 350$ nm, where the extinction coefficients of CDs remain constant as the sample changes physically (i.e., as surface groups interact with their surroundings in the course of transition of nanoparticles from one solvent to the other). Indistinct positioning of the isosbestic point of CDs in an acetone-water solution is attributable to the fact that acetone is an aprotic solvent and thus cannot form hydrogen bonds with surface groups of CDs. This „blurring" of the isosbestic point is one of the possible indicators of strength of hydrogen bonds in a system.

The presence of an isosbestic point in indicative of chemical equilibrium of the reaction (in the present case, reaction is understood as interactions of surface groups of CDs with solvent molecules in the process of substitution of one solvent with the other) at the given absorption wavelength and provides an opportunity to calculate the chemical equilibrium constant using the method outlined in [19]:

$$K = \frac{\mathrm{Opt(Isosbestic\ point)}}{[C_{\mathrm{water}}][C_{\mathrm{isopropanol/acetone}}]},$$

where Opt(Isosbestic point) is the optical density at the isosbestic point and C is the concentration of a solvent component in a suspension.

The calculated values of the chemical equilibrium constant fall within the range from 290 to 665. The range of variation of K is set by the presence of an isosbestic point in optical density spectra. In the case of CDs in a binary acetone-water solvent, the isosbestic point vanishes when the partial concentration of acetone exceeds 37.5% (Fig. 4, *b*). In a binary isopropanol-water solvent, the isosbestic point vanishes when the partial concentration of isopropanol goes above 75%. At isopropanol and acetone concentrations exceeding the indicated ones, no chemical equilibrium is found in the reaction of CD chromophores with solvent molecules. According to literature data, the reaction intensity is assumed to be moderate at $10^{-3} < K < 10^3$, and the amounts of residual reagents and reaction products are comparable [20]. Thus, one may conclude that when the solvent changes, the electronic levels of CDs shift gradually as water molecules get

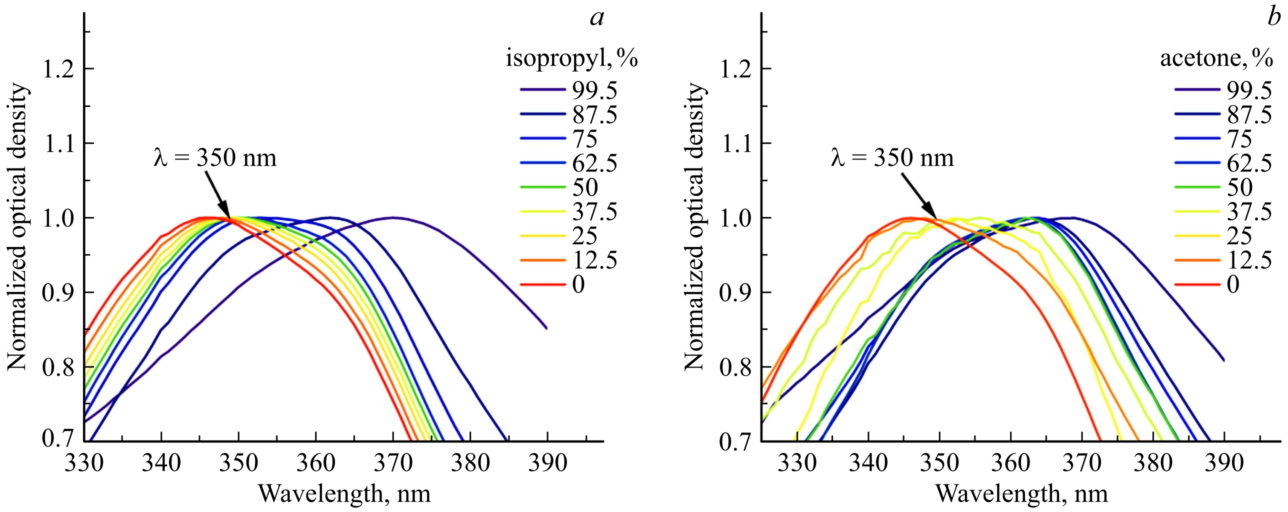

Figure 4. Normalized optical absorption bands of CDs in binary isopropanol-water (*a*) and acetone-water (*b*) solutions at different concentration ratios of solvent components.

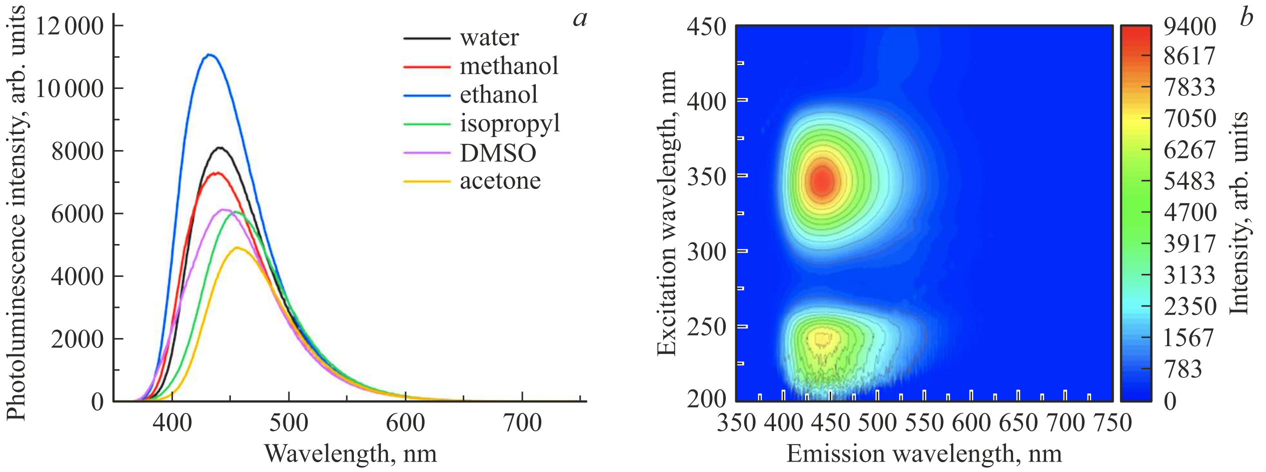

Figure 5. CD PL spectra in solvents under excitation at a wavelength of 350 nm (*a*) and CD PL excitation/emission matrix in water (*b*).

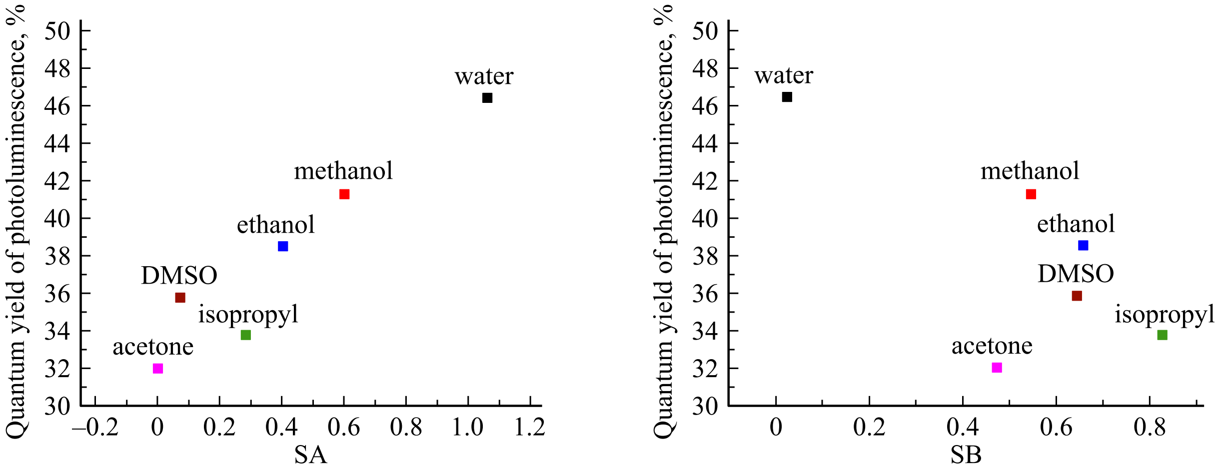

Figure 6. Dependences of the quantum yield of CD PL in solutions on the SA and SB values of the solvent.

substituted with molecules of the other solvent (isopropanol or acetone).

Photoluminescence spectroscopy

Figure 5, *a* presents the PL spectra of solutions of CDs in six examined solvents under excitation at a wavelength of 350 nm. This excitation wavelength was chosen for the fact that it corresponds to the maximum of the CD PL excitation spectrum (Fig. 5, *b*). It should be noted that the position of the PL band maximum and the PL intensity vary significantly from one solvent to another. The largest shift of the emission band maximum (30 nm) corresponds to CD PL bands in ethanol and acetone. CDs in these solvents also feature the highest and lowest photoluminescence intensities: the CD PL intensity in ethanol is 2.3 times higher than the one in acetone.

Dependences of the quantum yield of CD PL on the acidity and basicity of solvents (Fig. 6) were calculated in order to estimate the effect of solvents on the photoluminescent properties of CDs. The quantum yield of CD PL in water suspensions was determined using the reference dye method [18]. Quinine sulphate in a 0.05 M/L aqueous solution of sulphuric acid was used as a reference dye (its quantum yield of PL under excitation at a wavelength of 350 nm is 58% [18]).

The obtained results revealed that the quantum yield of PL increases with solvent acidity (this holds true for all the examined solvents) and decreases with increasing basicity of all solvents except acetone. Water, ethanol, methanol, isopropyl alcohol, and DMSO have nonzero acidity and basicity parameters, while acetone is a basic solvent. The positioning of the acetone point in the plot of dependence of the quantum yield of PL on SB suggests that the solvent acidity exerts a more significant influence on the fluorescent properties of CDs than the solvent basicity.

The observed growth of the quantum yield of PL with an increase in the solvent acidity is attributable to a change in the structure of electronic levels of CDs due to an increase in the number of protonated CD surface groups, which was illustrated by the IR and optical absorption spectra. This is yet another proof of the validity of our earlier data [3,21] revealing a significant influence of protonation of the surface of carbon nanoparticles on their PL.

Conclusion

CDs, which were synthesized hydrothermally from citric acid and ethylenediamine, were examined in six solvents with different acidity (SA) and basicity (SB) parameters: water, methanol, ethanol, isopropanol, DMSO, and acetone.

A significant dependence of the spectral characteristics of CD photoluminescence on solvent parameters (primarily its acidity SA) was revealed by analyzing the experimental data of IR and optical absorption spectroscopy and photoluminescence spectroscopy. It was found that the quantum yield of CD photoluminescence increases with increasing solvent acidity, while the energy of valence vibrations of polar bonds in surface CD groups decreases. The variation of optical properties of CDs with solvent acidity and basicity was attributed to the formation of hydrogen bonds between surface groups of nanoparticles and solvent molecules (as a result of protonation) and subsequent change in the structure of electronic levels of CDs. The existence of a chemical equilibrium of the reaction between CDs and solvents in binary water-isopropanol and water-acetone solutions upon gradual substitution of water molecules with isopropanol/acetone molecules in solution was revealed.

The obtained results contribute to the advancement of optical spectroscopy in the context of application of carbon dots in nanosensorics and technology processes.

Funding

This study was supported by grant No. 22-12-00138 from the Russian Science Foundation, https://rscf.ru/project/22-12-00138/.

Acknowledgments

Some of the experimental results used in this work were obtained using an IR Fourier spectrometer that was purchased under the Development Program of Moscow State University (agreement No. 65 dated October 04, 2021).

Conflict of interest

The authors declare that they have no conflict of interest.

References

[1] Y. Xu, C. Wang, H. Zhuo, D. Zhou, Q. Song. Nano Res, **16** (8), 11221–11249 (2023). DOI: 10.1007/s12274-023-5873-x

[2] B. Wang, H. Cai, G.I.N. Waterhouse, X. Qu, B. Yang, S. Lu. Small Science, **2** (6), 2200012 (2022). DOI: 10.1002/smsc.202200012

[3] M.Yu. Khmeleva, K.A. Laptinskiy, T.A. Dolenko. Opt. Spectrosc., **131** (6), 752–759 (2023). DOI: 10.21883/OS.2023.06.55913.104-23

[4] O.E. Sarmanova, K.A. Laptinskiy, S.A. Burikov, G.N. Chugreeva, T.A. Dolenko. Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, **286**, 122003 (2023). DOI: 10.1016/j.saa.2022.122003

[5] S. Wu, C. Zhou, C. Ma, Y. Yin, C. Sun. J. Chemistry, **2022**, 3737646 (2022). DOI: 10.1155/2022/3737646

[6] F. Yan, X. Sun, T. Ma, Y. Zhang, Y. Jiang, R. Wang, C. Ma, J. Wei, L. Chen, Y. Cui. Chemical Engineering J., **407**, 127801 (2021). DOI: 10.1016/j.cej.2020.127801

[7] B. Wang, S. Lu. Matter, **5** (1), 110–149 (2022). DOI: 10.1016/j.matt.2021.10.016

[8] A.M. Vervald, K.A. Laptinskiy, G.N. Chugreeva, S.A. Burikov, T.A. Dolenko. J. Phys. Chem. C, **127** (44), 21617–21628 (2023). DOI: 10.1021/acs.jpcc.3c05231

[9] X. Xu, G. Hu, L. Mo, Y. Li, H. Wei, B. Lei, X. Zhang, C. Hu, J. Zhuang, Y. Liu. Nanoscale, **13**, (2021). DOI: 10.1039/D0NR08128K

[10] S. Kazaryan, V. Nevolin, S. Pilosyan. Advanced Materials, 5–21 (2021). DOI: 10.30791/1028-978X-2021-8-5-21

[11] H.J. Lee, J. Jana, Y.-L. Thi Ngo, L.L. Wang, J.S. Chung, S.H. Hur. In Materials Research Bulletin, **119**, 110564 (2019). DOI: 10.1016/j.materresbull.2019.110564

[12] J. Catalan. In: *Handbook of Solvents* (ChemTec Publishing, Toronto, Canada, 2001).

[13] B.N. Tarasevich. *IK spektry osnovnykh klassov organicheskikh soedinenii. Spravochnye materialy* (Mosk. Gos. Univ., Khim. Fak., Kafedra Org. Khim., M., 2012) (in Russian).

[14] R.T. Morrison, R.N. Boyd. *Organic Chemistry* (Allyn and Bacon, Inc., Boston, 1967).

[15] Q. Zhang, R. Wang, B. Feng. et al. Nat. Commun, **12**, 6856 (2021). DOI: 10.1038/s41467-021-27071-4

[16] M. Xie, F. Zhang, H. Peng, Y. Zhang, Y. Li, Y. Xu, J. Xie. Colloids and surfaces. B, Biointerfaces, **176**, 462–470 (2019). DOI: 10.1016/j.colsurfb.2019.01.028

[17] A.N. Emam, S.A. Loutfy, A.A. Mostafa, H. Awad, M.B. Mohamed. RSC Adv., **7**, 23502–23514 (2017). DOI: 10.1039/C7RA01423F

[18] J.R. Lakowicz. *Principles of Fluorescence Spectroscopy* (Springer, 2006).

[19] S. Hemdan, A. Mansour, F. Ali, Almandumah. Journal of Science and Human Studies, **62**, 1–21 (2019). DOI: 10.37376/1571-000-062-004

[20] B. Averill, P. Eldredge. *General Chemistry: Principles, Patterns, and Applications* (Saylor Academy, 2012).

[21] A.M. Vervald, A.V. Lachko, O.S. Kudryavtsev, O.A. Shenderova, S.V. Kuznetsov, I.I. Vlasov, T.A. Dolenko. J. Phys. Chem. C, **125** (33), 18247–18258 (2021). DOI: 10.1021/acs.jpcc.1c03331

Translated by D.Safin