



Communication

Temperature-Dependence of Solvent-Induced Stokes Shift and Fluorescence Tunability in Carbon Nanodots

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Abstract: We carried out a cryogenic investigation on the optical properties of carbon dots, aiming to better understand their emission mechanism and the role of the solvent. The solvatochromic Stokes shift is quantified by a low temperature approach which allows freezing of the photo-excited state of carbon dots, preventing any solvation relaxation. Moreover, the reduction in temperature helps to identify the dynamical inhomogeneous contribution to the broadening of the emission band; therefore, disentangling the role of solvent from other types of broadening, such as the homogeneous and the static inhomogeneous contributions.

Keywords: carbon nanodots; fluorescence tunability; cryogenic optical study

1. Introduction

Carbon dots (CDs) are one of the most relevant and novel materials which appeared recently in nanomaterials science [1–4] and are currently attracting substantial interdisciplinary research interest [2,5–7]. They are small, surface-functionalized carbonaceous nanoparticles displaying interesting optical properties, such as a bright fluorescence which is usually tunable across the visible range as a function of the excitation wavelength [8–10]. The combination of these characteristics with non-toxicity, low fabrication cost and ease of synthesis, makes CDs extremely promising for several photocatalytic, [7,11,12] optoelectronic [6] and biological applications [6,7,13,14]. However, several important questions remain open on the optical response of CDs such as, for example, their interaction with the external environment and the origin of fluorescence tunability.

In fact, it is well known that the surface of CDs has a key role in the emission mechanism, causing a strong interaction between the dot and, for example, solvent molecules and ions or molecules in solution [15–18]. One way to investigate these processes arising from the interaction with the external environment is the study of the fluorescence at low temperatures. Several studies have highlighted the strong influence that solvent relaxation bears on the emission energy of CDs, due to the increased polarity in the excited electronic states [19–21]. Interestingly, lowering the temperature should allow observation of the emission from an excited state which is frozen in a non-equilibrium state and which is not yet relaxed, thus eliminating any solvation relaxation or broadening of the band, which usually occurs in a few picoseconds [15]. Besides, this approach should also allow disentangling of any contribution to fluorescence tunability that arises from solvent relaxation effects [22]. However, temperature-dependent studies of CD emission are almost non-existent in the literature. The previous few studies on CD emission at low temperatures [23–25], showed that the fluorescence band changes its intensity as a function of temperature but undergoes limited shift or narrowing. In a recent paper, the observations that CD emission remains very broad and strongly Stokes-shifted from

excitation even at cryogenic temperature, together with the lack of absorption-emission mirror symmetry, were interpreted as evidence of CD emission being due to the dynamic formation of self-trapped Frenkel excitons in the core structure [25]. Here, we studied the emission characteristics of CDs at 300 K and at 80 K, dissolved in glycerol and photo-excited at different excitation wavelengths. Our study confirms the importance of solvation in the emission mechanism and provides new insight on the photophysical mechanisms contributing to the characteristic tunability of CD fluorescence.

2. Materials and Methods

2.1. Synthesis

The synthesis of carbon dots (CDs) is based on the microwave-induced decomposition of an aqueous (milliQ, 10 mL) solution of citric acid (3 g) and urea (3 g) (Sigma Aldrich, Milan, Italy), which has already been described in detail in our previous work [26]. The synthesis results in monocrystalline carbon nanoparticles 1–6 nm in size, with a carbon nitride core structure in the β crystalline configuration, and rich in polar groups on the surface as carboxylic and amide groups [26].

2.2. Steady-State Absorption

Absorption measurements were carried out on samples prepared by dissolving the as-prepared CD nanopowders in glycerol (Sigma Aldrich, Milan, Italy) in a concentration of 0.01 g/L. The absorption measurements were performed by a double beam spectrophotometer (JASCO V-560, Japan) in the 220–700 nm range in a 1 cm quartz cuvette. All the measurements were performed at room temperature.

2.3. Steady-State Fluorescence

Fluorescence measurements were performed on a solution of CDs in glycerol (0.01 g/L), and in 1,4-dioxane (Sigma Aldrich, Milan, Italy) in a concentration of 0.005 g/L. The emission spectra were recorded with a JASCO FP-6500 spectrofluorometer (JASCO, Japan) in a 1 cm cuvette with a 3 nm resolution bandwidth. The first set of measurements was performed at room temperature. An additional set of measurements was conducted at low temperatures with the use of an Oxford Instruments cryostat (Oxford Instrument, UK) under a liquid nitrogen flow. The sample of CDs suspended in glycerol was positioned in a quartz cuvette in thermal contact with the cold finger of the cryostat. Once the cryostat was evacuated and brought to cryogenic temperatures, the glycerol formed a glass, trapping CDs, thus allowing good-quality optical measurements at 80 K. The QY value of CDs in glycerol was estimated by comparing the steady-state emission intensity with that obtained from an aqueous solution (pH = 13) of fluorescein excited at 470 nm, used as a reference of known QY = 95%.

3. Results and Discussion

A solution of CDs in glycerol was prepared at the concentration of 0.01 g/L, and its absorption collected at room temperature is shown in Figure 1. The main feature appearing in the spectrum is a broad band peaking around 410 nm, with a clear tail extending at long wavelengths. This band is associated with the lowest-energy electronic transition of the nanoparticles and is the one mostly responsible for the characteristically strong fluorescence of CDs. The emission efficiency (quantum yield) was estimated by a comparison method and it results $\approx 25\%$.

The solution was photoexcited at various excitation wavelengths and the normalized emission spectra are reported in Figure 1. They show the typical tunability associated with CD emission bands, which consists of a continuous shift of the emission peak following the change of the excitation wavelength. A closer look at these data, and a quantitative comparison between the excitation and emission energies, reveals such a shift is not a rigid one. In fact, the excitation-emission Stokes shift ($SS = \text{Excitation energy} - \text{emission energy}$) is strongly excitation-dependent. In particular, from the data in Figure 1 it can be seen that the SS is more pronounced at lower excitation wavelengths. For

example, the shift amounts to ≈ 110 nm (that is, $SS = 0.64$ eV) if the sample is excited at 410 nm (3.02 eV), and to only 35 nm ($SS = 0.15$ eV) if the sample is excited at 525 nm (2.36 eV). Because most of this SS is due to solvation as explained below, this behavior suggests a progressive decrease in the excited-state dipole moment for CDs excited at increasingly longer wavelengths.

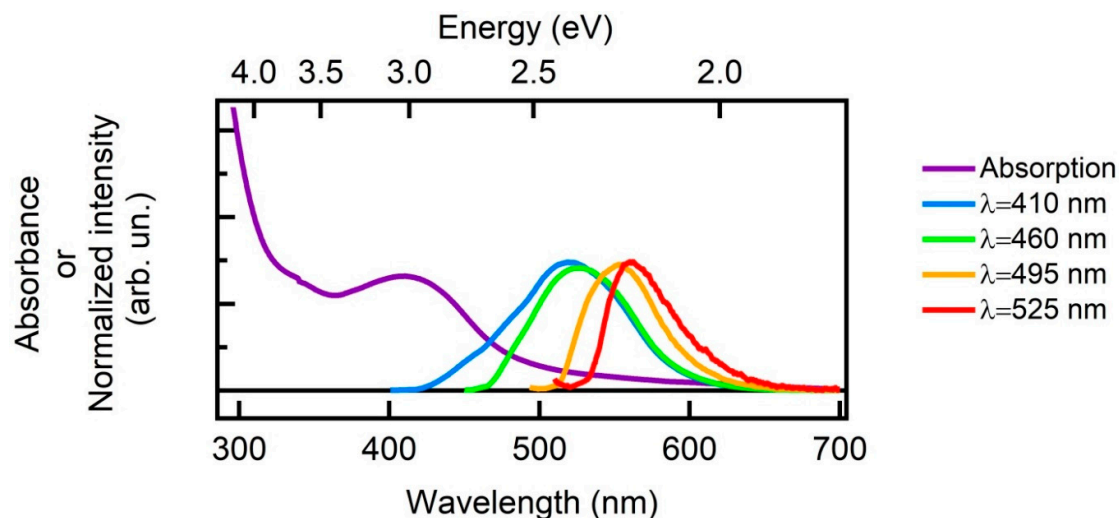


Figure 1. Absorption spectrum of CDs dissolved in glycerol (purple curve), normalized emission spectra of CDs in glycerol excited at 410 nm (blue curve), 460 nm (green curve), 495 nm (orange curve) and 525 nm (red curve).

In a previous study [19], we demonstrated the strong solvatochromic behavior of the emission of these CDs highlighted by the regular redshift of the band with the increase of solvent polarity which includes both the contribution of dielectric constant and the hydrogen bond capability. In fact, such behavior provides strong evidence that the emission of these CDs involves surface-localized transitions. Therefore, in the present case the emitting state can be pictured as a surface-localized exciton [15,19], rather than a self-trapped exciton [25]. Here, CDs are dissolved in glycerol, which is a strongly polar solvent. In fact, glycerol has a dielectric constant $\epsilon = 43$ and, considering its three –OH groups, it is expected to establish strong hydrogen bonds with acceptor groups, such as carboxylic and amide groups, on surface of the dot [27]. For these reasons, it is suggested that a great part of the Stokes shift shown in Figure 1 could be attributed to the solvation relaxation of the excited state.

Thus, in order to investigate these phenomena in more detail, steady state fluorescence experiments were repeated, also at 80 K. In fact, cooling down the temperature should stop the occurrence of solvation because the excited state is frozen in a non-relaxed configuration. In addition to this, temperature may also have an effect on emission band broadening, which could otherwise be hiding, for example, the presence of vibrational sub-structure in the emission bands.

Generally speaking, the bandwidth of a fluorescence signal arises from a combination of three contributions: (i) static inhomogeneous broadening (σ_{s-in}) due to dot-to-dot fluctuations of the emission energy, (ii) dynamic inhomogeneity (σ_{d-in}) due to solvent-related fluctuations, and (iii) homogeneous broadening effects (σ_h) due to the coupling of the electronic transition with vibrational modes. In particular, low temperature should substantially reduce the portion of the homogeneous broadening due to coupling with soft vibrational modes, as well as the solvent-dependent inhomogeneous broadenings of the emission band, because it hinders solvent fluctuations. In fact, the expected amount of inhomogeneous broadening due to solvation is directly connected to the solvatochromic Stokes shift. Theoretically, the two are related by $\sigma_{d-in} = (\Delta E \times k_B T)^{1/2}$ [28], where ΔE is the energy shift of the emission due to solvation (ΔE equals solvation-induced SS if there are no solvation effects on the absorption band).

In Figure 2 the emission spectra recorded at 80 K are compared with those acquired at room temperature. We observe that the SS recorded at low temperatures is significantly smaller than the SS recorded at room temperature, suggesting the disappearance of solvation-induced redshift contributions. For example, when exciting CDs at 410 nm, the SS changes from 0.64 eV (110 nm), measured at 300 K, to 0.41 eV (64 nm) measured at 80 K. Therefore, these data demonstrate that at least half of the SS measured at room temperature is due to solvent interactions, confirming the strong sensitivity of CDs to the environment. Assuming that solvent relaxations have been completely eliminated at cryogenic temperature, the residual SS measured at 80 K should be entirely due to internal energy relaxation of the photo-excited dot, not involving the interaction with the environment. In other words, the residual SS should entirely be due to vibrational relaxation, due to the coupling with high-frequency vibrational modes, or any internal conversion processes which can occur in the sub-nanosecond range after photoexcitation.

Interestingly, we find that the disappearance of the solvent-induced SS has a beneficial effect on CD fluorescence tunability. In fact, in Figure 2c the emission peak is plotted as a function of excitation energy, clearly demonstrating that at low temperature the degree of tunability is increased, considering that the emission energies span a larger spectral range with respect to the higher temperature; while at room temperature CD emission spans from 560 nm (2.21 eV) to 520 nm (2.38 eV), when the excitation is moved from 525 nm (2.36 eV) to 410 nm (3.02 eV), CDs at 80 K display more than twice the degree of tunability, considering that their emission spans from 560 nm (2.22 eV) to 474 nm (2.61 eV) for the same range of excitations. The magnitude of the SS for different excitation and temperatures are summarized in Table 1.

The vertical distance between the two sets of points in Figure 2c (or, equivalently, the difference between the SS at 300 K and 80 K, as shown in Table 1) can be taken as an estimate of the solvation-induced contribution to the SS. Therefore, the fluorescence is more tunable at low temperature because of the disappearance of the solvation-induced redshift which partially compensates for the intrinsic shift of CDs when tuning the excitation. Besides, the values in Table 1 highlight again that the effects of solvation progressively move to zero for CDs excited at lower energies.

Table 1. Values of the excitation-emission Stokes shift (eV) for CDs in glycerol excited at different energies, as detected at two different temperatures.

Excitation Wavelengths (nm)	80 K	300 K	Excitation Energies (eV)
410	0.41	0.64	3.02
460	0.21	0.33	2.70
495	0.18	0.22	2.51
525	0.14	0.15	2.36

It is already known from previous works [15,29] that the tunability can be essentially interpreted as a photo-selection effect, ultimately related to a manifold of quasi-identical electronic transitions peaking at slightly different energies, associated with an inhomogeneous distribution of non-equivalent CDs. Based on the observed solvent response, we can infer that exciting any of these transitions generates a non-zero electrical dipole moment which is able to interact with the external environment as, for example, with solvent molecules. However, the present data reveal that the magnitude of the photo-excited dipole moment is not a constant across the manifold of tunable transitions. In fact, when looking at how the SS depends on the excitation wavelength (Figure 1) it is evident that the solvatochromic shift is dependent on the excitation energy and, in particular, it is larger at higher excitation energy. The results in Figure 2 further support this view. In fact, at lower excitation energies, the difference between the emission band at high and low temperature almost disappears, confirming that the solvatochromic shift is almost null at low energies. This suggests that the size of dipole moment which characterizes the excited state decreases along the manifold, thus reducing the interaction with the solvent and, therefore, the Stokes shift.

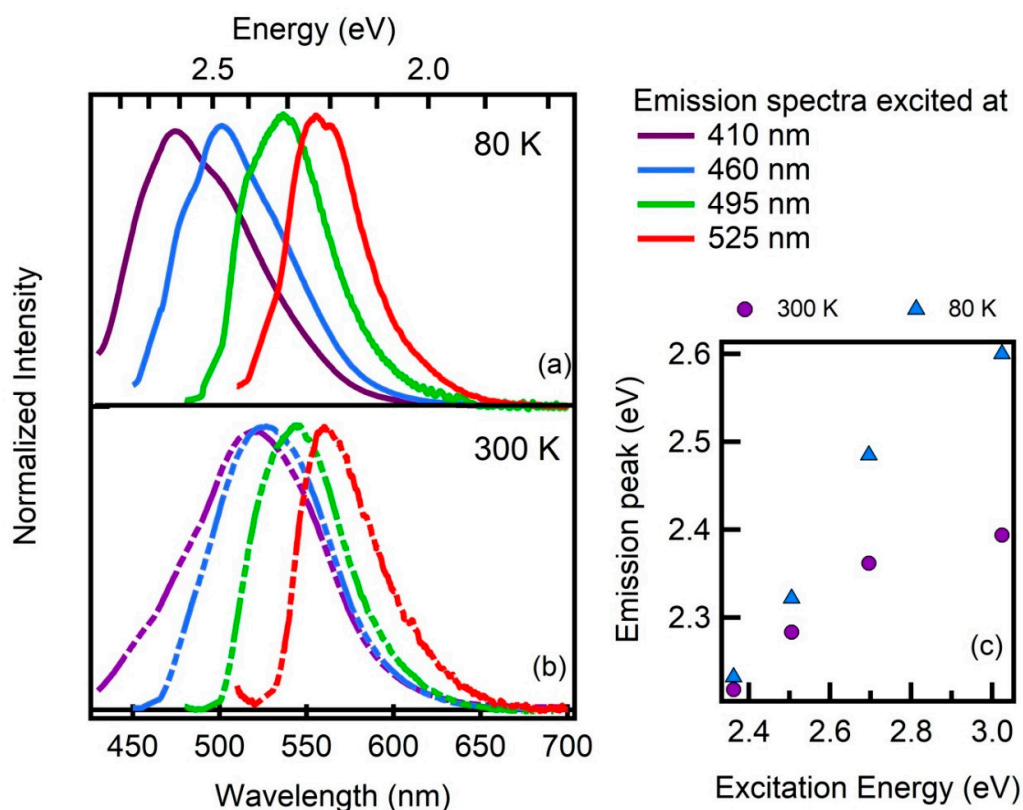


Figure 2. Normalized emission spectra of CDs in glycerol excited at 410 nm (purple curve), 460 nm (blue curve), 495 nm (green curve) and 525 nm (red curve) performed at 80 K (a) and 300 K (b); (c) emission peak as a function of excitation energy.

In order to further confirm the role of solvation in the shift of the emission band, we also compared the spectra in glycerol with that of CDs in dioxane (Figure 3). Dioxane was chosen here because it is the most apolar solvent (dielectric constant $\epsilon \approx 2.3$) in which these CDs can be well dissolved. Considering its low polarity, we can assume that the effects of solvation can be neglected in this case. Comparing the emission bands in glycerol and dioxane at room temperature (Figure 3, green and red curves), indeed, the peak is redshifted at almost 50 nm (0.23 eV) in glycerol with respect to dioxane, again underlining the role of solvation. However, when decreasing the temperature to 80 K, the emission band of CDs in glycerol perfectly matches the one in dioxane (Figure 3 green and purple curves), which conclusively proves that a temperature of 80 K is low enough to completely turn off solvation effects in a glycerol environment.

On the other hand, the data in Figures 2 and 3 also reveal that the width of the emission bands in glycerol is almost unchanged from 300 K to 80 K. This indicates that the contribution of solvent-induced inhomogeneous broadening to the overall bandwidth is essentially negligible. This is particularly evident by the fact that the band remains quite broad (Figure 3) even in dioxane, where solvation effects should be almost zero. Using the equation $\sigma_{d-in} = (\Delta E \times k_B T)^{1/2}$, [28] one can estimate the amount of inhomogeneous broadening due to solvation. From the data in Figure 3, we can estimate ΔE as the shift between dioxane and glycerol at 300 K, that is approximately 0.23 eV. From that, we obtain $\sigma_{d-in} = 0.077$ eV, which is indeed much smaller than the overall width of about 0.4 eV observed in Figure 3.

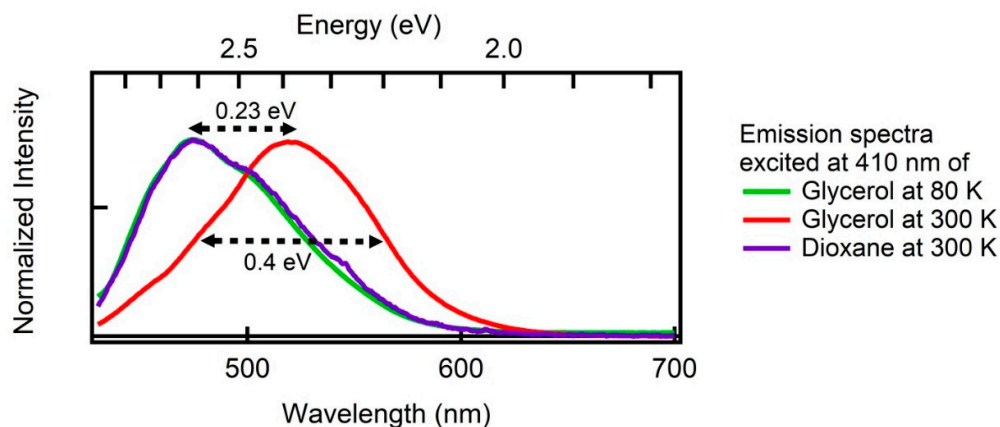


Figure 3. Normalized emission spectra of CDs excited at 410 nm in glycerol at 80 K (green curve), in glycerol at 300 K (red curve) and in dioxane at 300 K (purple curve).

Therefore, although solvation has a dramatic effect on the peak position of the emission, it hardly influences the shape of the bands. The latter is controlled by a combination of homogeneous broadening, due to the coupling to vibrations, and static inhomogeneity, due to dot-to-dot fluctuations of the emission energy. As a matter of fact, the shape of the low-temperature signals reported in Figure 2a hints at the appearance of a sub-structure, which may be a manifestation of the vibrational structure hidden under the broad emission band. Estimating the energetic separation is quite complex, considering that the emission has been detected after passing through a bandpass filter which absorbs strong scattered light. Nevertheless, the sub-structure remains scarcely visible, suggesting that static inhomogeneity remains the dominant source of broadening.

4. Conclusions

By analyzing the characteristics of the emission of CDs at room and cryogenic temperature, and by comparing the shape of CD emission bands in a polar and an apolar solvent, we showed that the majority of the excitation-emission Stokes shift in CDs suspended in a polar solvent is due to solvent relaxation in the photo-excited state, and we showed that these relaxations completely disappear at a temperature of 80 K. Besides, we found that the influence of solvent-induced inhomogeneity effects on the emission shape of CDs is almost negligible, the latter being mostly controlled by static inhomogeneity. Finally, we provided evidence that solvent-induced Stokes shift works against the characteristic tunability of CD fluorescence, and the latter is strongly enhanced at low temperatures, when the solvent is frozen. These results may pave the way to strategies capable of selectively enhancing or suppressing the tunability of CD fluorescence, which may be useful for several applications.

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Conflicts of Interest: The authors declare no conflict of interest

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