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Markedly Enhanced Photoluminescence of Carbon Dots Dispersed in Deuterium Oxide

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Abstract: In this work we report some surprisingly interesting results in our pursuit to improve the photoluminescent emission of Carbon Dots (CDs) prepared from various precursors. By simply replacing the regular water with deuterium oxide (D₂O) as dispersion medium, the emission intensity and the subsequent quantum efficiency of the radiative processes could be markedly enhanced. The present study was performed on our previous reported works related to CDs; in each case the preparation path being maintained accordingly. For each type of CDs, the emission intensity and the absolute photoluminescence quantum yield (PLQY) were highly improved, in certain cases more than doubled values being recorded, the gain in performance being easily remarked with the naked eye even in plain daylight. For each type of CDs dispersed in regular water and heavy water respectively, the photoluminescent properties were thoroughly investigated through Steady State, Lifetime and absolute PLQY. To further elucidate the mechanism involved in the photoluminescence intensity enhancement, samples of D₂O and H₂O dispersed CDs were embedded in a crosslinked Poly(acrylic acid) polymer matrix. The investigations revealed the major influence of the deuterium oxide dispersion medium over the PL emission properties of the investigated CDs.

Keywords: carbon nano dots; photoluminescence; deuterated mediums.

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1. Introduction

Photoluminescent Carbon Dots (CDs) are a newer established class of carbon materials which gained a lot of research interest in the last decade due to their high application potential in optoelectronic devices, sensors and medical investigations [1,2,3] or even food sciences [4]. One of their particular properties is the observed emission peaks dependence on the excitation wavelength which triggered a lot of debate regarding the involved photoluminescence mechanisms. To date, it is still an open debate subject being generally accepted the contribution of both the defect rich π -bond conjugated graphitic like configuration of the carbon core and the radiative transitions arising from the surface located functional groups [5,6,7]. While the first study regarding the influence of deuterium substitution of hydrogen in naphthalene over its phosphorescence arising from triplet states is dated in the beginning of 60's [8], to date there are still a limited number of studies regarding this matter. More recently, the benefit of deuterated water over the luminescent emission was studied in a wider range of fluorescent dyes [9,10] the results being impressive since the enhancement of the recorded PL intensity varies within 30-70% range. A

similar effect of increasing the fluorescent intensities induced by deuterium oxide was reported for intercalated dyes as fluorochromes bound to DNA [11], or in case of liquid chromatography with fluorescence detection [12]. The presence of deuterium in various dyes, proteins, and lanthanide compounds is also able to produce a notable enhancement of their luminescent emission [13]. Also, in the pursuit of improving the performance of the OLED displays in terms of efficiency and long-term operational stability, hydrogen replacement with deuterium in TADF/AIQ/Q2AIOAr emitters was found to be highly effective in achieving these goals [14,15]. In a very recent study, CDs prepared from citric acid via a hydrothermal route were dispersed both in water and deuterium oxide, a similar markedly increased emission being recorded. Thus, the PLQY values were doubled in case of D₂O prepared CDs, the structural analysis revealed, according to the authors, the replacement to a certain extent of hydrogen with deuterium within the CDs structure [13-16] which provide, in their view, a decisive contribution in achieving the overall emission intensity improvement. As will be further presented, our investigation does not necessarily sustain the claim regarding the significant contribution of the H to D substitution within the CDs structure to the observed emission intensity improvement. While, the effective deuteration of the CDs might play a significant role in achieving better PLQY, the particular conditions provided by the D₂O dispersion medium environment is, in our opinion, the main trigger of the markedly enhanced emission efficiency. In this work, CDs prepared through thermal processing of some imide precursors and argan waste were dispersed in deuterium oxide and further investigated through Steady State, Lifetime and PLQY fluorescence. For gathering more information regarding the role of D₂O in achieving the recorded enhancement of photoluminescent emission, the CDs dispersions were further embedded in a crosslinked Poly(acrylic acid) polymer matrix. The reported results could bring additional evidence in the pursuit of definitive elucidation of the specific PL mechanisms of CDs and also an interesting approach for their applications in optoelectronics, sensors, medical imaging where as high as possible emission intensity is often required. Also, given the observed markedly enhanced PL emission in D₂O medium, this study may trigger further interest in research related to deuteration and deuterated mediums.

2. Materials and Methods and Preparation

2.1. Materials

N-Hydroxyphthalimide (NHF) (97%), N-Hydroxysuccinimide (NHS), anhydrous ferric chloride (FeCl₃), acrylic acid (AA), *N,N'*-Methylenebisacrylamide (MBAM), 1-Hydroxycyclohexyl phenyl ketone (HCPK), deuterium oxide (D₂O), ethanol (EtOH) were sourced from Merck Chemicals. Argan cake waste obtained during argan oil preparation through cold pressing was provided by a local Moroccan co-operative. Ultra-pure distilled water (Millipore-Direct Q) was used during preparation stages.

2.2. Methods

Freshly prepared samples were investigated through steady-state fluorescence, the emission spectra were recorded on a Horiba Fluoromax 4P spectrofluorometer (Horiba Ltd., Kyoto, Japan). In each case of pair investigation (H₂O vs D₂O) the measurement parameters (entrance/exit slits and integration time) were kept unchanged. The absolute photoluminescence quantum yield (PLQY) values were recorded with the Quanta Φ integration sphere controlled by the Horiba spectrofluorometer according to the equipment manufacturer's procedure using FluorEssence software (ver. 3.5.1.20) for spectral acquisition and subsequent calculations of the QY and CIE1931 parameters. Excited states lifetimes (LT) were investigated on the same equipment with the attached Horiba Lifetime module using a 370 nm LED excitation source. Dimensional analysis (DLS) was performed on a Malvern Panalytical Zetasizer Advance Pro Red (Malvern Panalytical Ltd UK). Freshly prepared and 1-week aged dispersions were investigated.

2.3. Preparation

Each type of CDs was prepared according to experimental approach detailed in our previous works. Briefly, NHF (NHF-CDs) [17], NHS (NHS-CDs) [18], argan waste CDs (AW-CDs) [19] and NHF-Fe(III) complex (Fe-CDs) [20], were prepared by thermal processing of the respective precursors, followed by dispersion in H₂O and D₂O and further centrifugation, purification and dimensional selection. In case of Fe(III) doped CDs (Fe-CDs), additional steps for preparation/purification of the intermediate Fe(III)-NHF complex is required. For the embedment of the CDs in the polymer matrix the following experimental procedure was followed: in each 1,5 mL of freshly prepared NHF-CDs dispersed in D₂O and H₂O respectively, 140 mmol AA and 2 mmol MBAm (as crosslinker) were dissolved under stirring followed by the addition of 0,1 mmol of HCPK (as photoinitiator). Then the mixture is transferred in a convenient shaped

container and further photopolymerized through exposing to an UV-A (360-370 nm) source. The photopolymerization process is fast (under 60 s) depending on the UV-A source type (in our case a 365 nm LED array was used).

3. Results and Discussion

One of the most interesting and sought after features of CDs is their PL emission which is excitation wavelength dependent in most reported cases. Besides the type of precursors and the chosen preparation route, their PL emission characteristics are strongly dependent on the dispersion environment, the solvent or the polymer matrix types being key factors in terms of PL emission efficiency and location of the emission peaks [17,21]. The PL mechanism of CDs is still an open debate subject with a general opinion in favor of both contribution of the defect rich disordered graphitic core and the radiative transitions arising from the surface located functional groups [22]. As mentioned above, there are several studies regarding the influence of deuteration over the emission intensity of CDs or other fluorophores where the "isotope effect" is highlighted as the main reason of the observed emission enhancement [16,23]. According to our study, there are several observations worth mentioning regarding this approach: (a) spontaneous H → D exchange might occur for a certain functional groups especially in case of organic fluorophores (-OH, NH) when solved in D₂O but less probable in case of CDs where the highly packed carbonaceous core involves bonding stability achieved through high temperature carbonization of the precursor; (b) deuteration is more likely to occur in the surface located functional groups attached to the carbonaceous core of the CDs especially when the hydrothermal (with D₂O instead of H₂O as processing medium) route is used for their preparation; (c) CDs obtained through the wider spread route of direct thermal exposure (pyrolytic or not) of the precursor is less capable of sustaining a H → D exchange since the CDs are already structurally stable within the D₂O dispersion medium. In this case, a preliminary stage of H → D exchange within the precursor might provide a certain level of structural deuteration of the resulted CDs. Generally, the efficiency of the radiative transitions could be markedly affected by the surroundings of the emissive species. In aqueous dispersions the efficiency of the radiative processes is lowered by the vicinity of the OH oscillators favoring vibrational coupling which provide an efficient non-radiative deactivation path of the excited states [24,25]. Given the configuration of the CDs with their multiple emission sites located within the carbonaceous core or in the surface attached functional groups it is expected that the overall efficiency of the radiative processes to be strongly affected. By switching water to deuterium oxide provide a more favorable surrounding where the non-radiative deactivation paths are markedly diminished thus favoring the radiative relaxations through photon production. Given the particularities of D₂O [26] which dissociates less than H₂O and the new vibrational conditions due to the presence of the heavier deuterium providing a better environment for the photonic processes within the CDs. Therefore, in our view and due to the investigations results detailed here, the isotope effect plays an indirect role in enhancing the PL emission by providing a more favorable environment for the radiative transitions.

3.1. Photoluminescence investigation

3.1.1. Steady State Fluorescence investigation

For each investigated type of CDs, the spectra were recorded at 3 excitation wavelengths (330, 350, 370 nm), same equipment measuring parameters (entrance/exit slits, integration time etc) being kept unchanged. In Figure 1 are presented the recorded spectra recorded for NHF-CDs dispersions in H₂O and D₂O respectively, while the embedded pictures (recorded using a commonly available laboratory 370 nm UV lamp) could provide a clear view regarding the visually perceived emission intensity difference between the two samples. As could be noted, the recorded spectral intensity at any excitation wavelength is at least 2.4x higher in case of NHF-CDs dispersed in D₂O which is consistent with the visually perceived observation. In both cases the location of the peaks remained practically unchanged irrespective of the excitation wavelength, the most intense peaks being recorded at 370 nm excitation.

In case of the NHS-CDs (Figure 2) the emission intensity enhancement in the D₂O environment is still significant (both instrumental and visual) but not as impressive as observed in the previous situation. Overall, the emission intensity of this type of CDs is markedly lower compared with the NHF-CDs (please note the entrance/exit slits values), but still 1.2x higher for the NHS-CDs dispersed in D₂O. The recorded emission peaks remain unchanged at 350, 370 nm excitation with a minor difference (414 to 417 nm) being noted at 330 nm excitation. The maximum intensity peaks were in both cases recorded at 350 nm excitation.

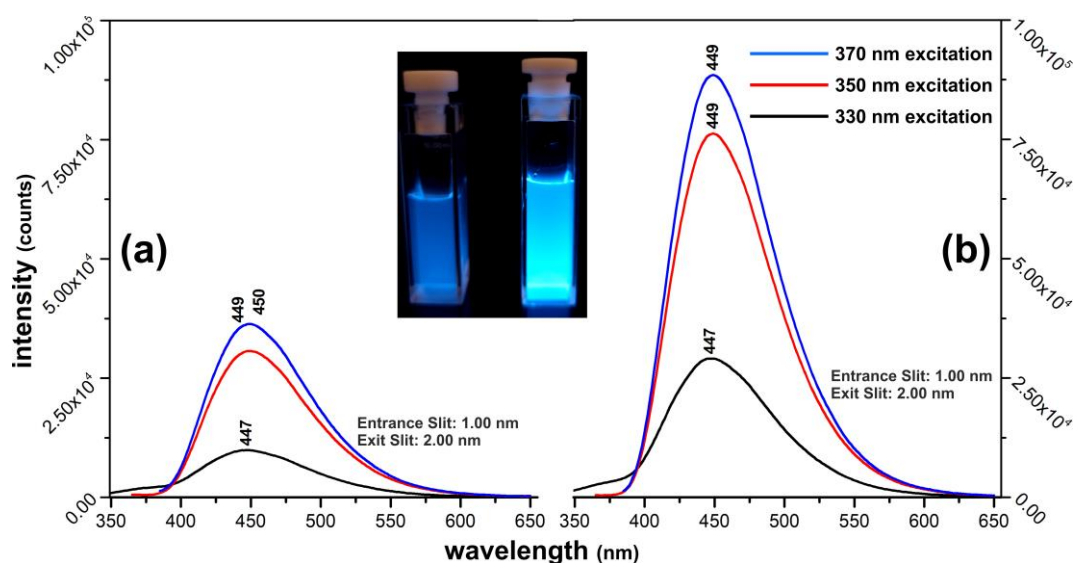


Figure 1. PL emission of the NHF-CDs dispersed in (a) water, (b) deuterium oxide.

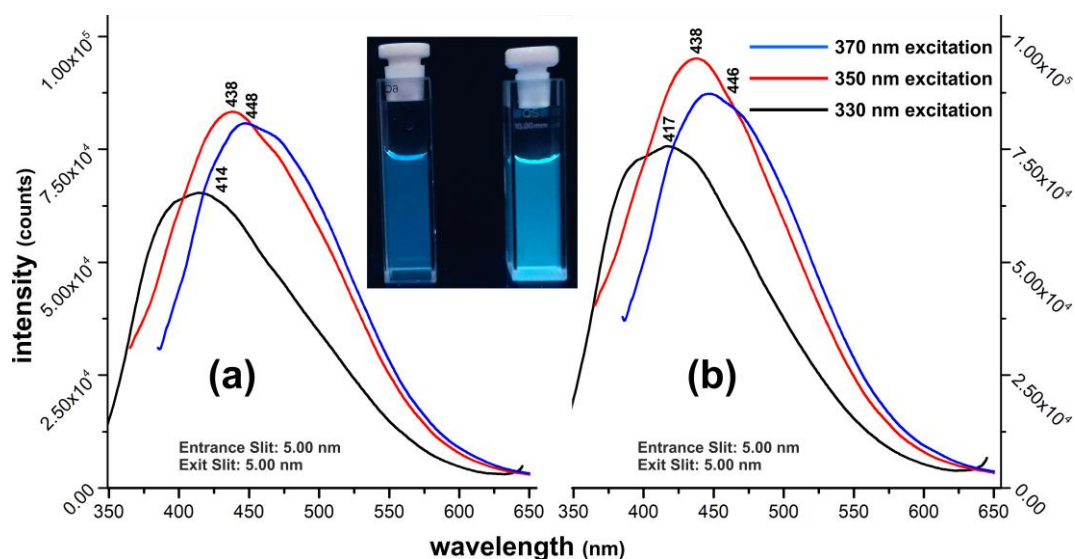


Figure 2. PL emission of the NHS-CDs dispersed in (a) water, (b) deuterium oxide.

The AW-CDs (Figure 3) displayed a similar behavior as the NHS-CDs with a clearly enhanced emission recorded for the D₂O dispersions. In both cases (H₂O and D₂O dispersions) the most intense peaks are recorded at 370 nm excitation wavelength, their location being unchanged at 350 nm excitation with a slight difference (414 to 417 nm) recorded at 330 nm and (448 to 446 nm) at 370 nm excitation wavelength. In all cases, the observed unchanged location of the emission peaks (in H₂O and D₂O dispersions) are consistent with other reported works where the emission peaks in deuterated solvents show no significant shift [6].

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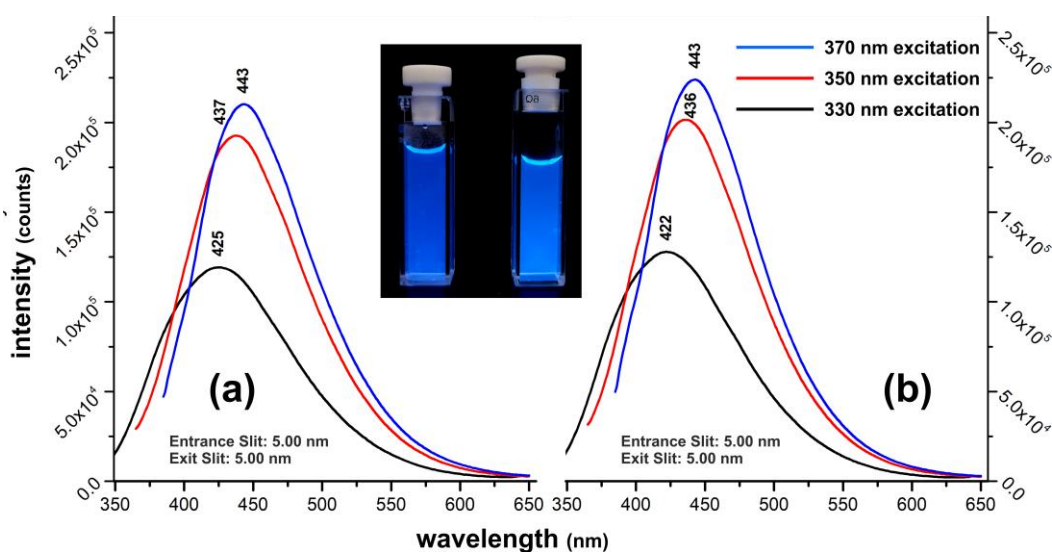


Figure 3. PL emission of the AW-CDs dispersed in (a) water, (b) deuterium oxide

The green emitting Fe(III) doped CDs prepared by thermal processing of a Fe(III)-NHF complex present also a markedly enhanced emission when dispersed in D₂O (Figure 4). As could be noted, the enhanced emission intensity is highlighted both instrumentally and visual. The recorded emission intensity is at least 1.6x higher in D₂O dispersion at all investigated excitation wavelengths, the most intense emission being achieved at 350 nm excitation. Practically, there are no differences between emission peaks, the variations (+/- 1 nm) could be safely attributed to the inherent measuring and/or results interpretation errors.

As mentioned above, the recorded results for all four types of prepared CDs led to the conclusion that the enhancement of the PL emission intensity is rather a result of more favorable conditions achieved in the D₂O dispersion environment which provide significantly less non-radiative vibrational deactivation routes compared with H₂O dispersions. In our view, the “isotope effect” could be only indirectly used to provide a convincing insight regarding the generally observed PL intensity enhancement.

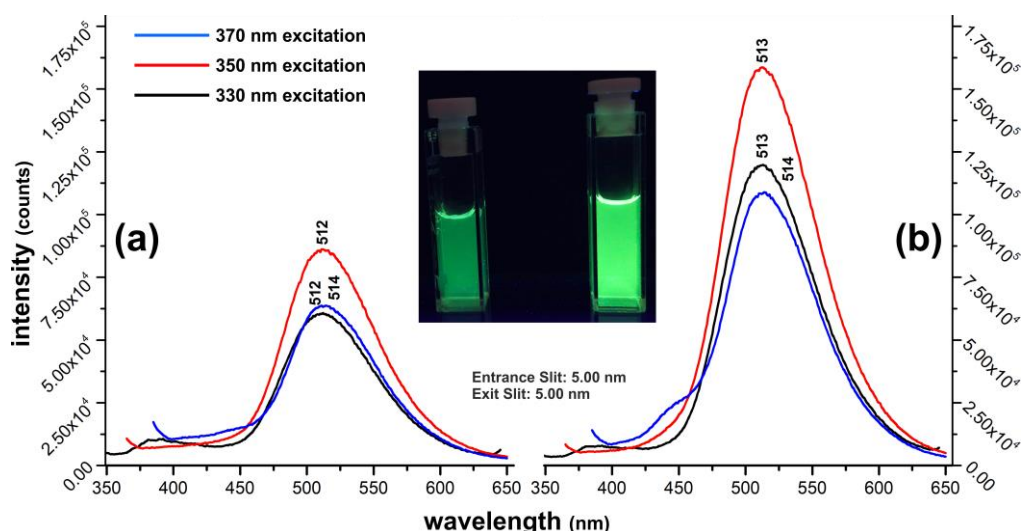


Figure 4. PL emission of the Fe-CDs dispersed in (a) water, (b) deuterium oxide

To further strengthen the above-mentioned observations, we also investigated the behavior of both NHF-CDs dispersions in D₂O and H₂O when embedded in a polymer matrix (Chapter 2.3.). Changing the surroundings of the NHF-CDs could be a good test of the hypothetic contribution of H → D exchange within the CDs structure. In Figure 5 are presented the observed PL intensities of the NHF-CDs/monomer/crosslinker /photoinitiator in D₂O mixture just after the

commencing of the photopolymerization process (a) and post-polymerization when a solid nanocomposite of NHF-CDs trapped in the crosslinked polymer matrix is obtained (b). While within the initial 0-5 seconds after the UV exposure of the mixture the characteristic blue emission of the NHF-CDs is intense, it become gradually fainter to the end of the photopolymerization when the polymer matrix is completely established with the CDs trapped within. The entire process is demonstrated in the short video file (V1) attached to the manuscript. Due to the fast polymerization process (within a 40 s interval) the diminishing PL blue emission is clearly noticeable being most probable a result of changing the emissive sites surrounding conditions. At the end of the process, the initial quantity of D₂O of the mixture is mostly expelled, the crosslinked polymer matrix backbone being the new surrounding environment for the NHF-CDs.

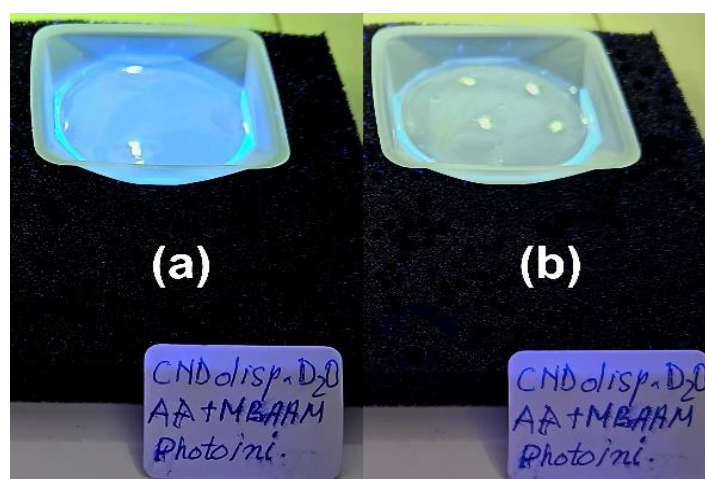


Figure 5. Observed PL emission intensity of the NHF-CDs/ monomer/crosslinker/photoinitiator/D₂O mixture (a) prior and (b) post-polymerization

3.1.2. PLQY Measurements

The PLQY investigation revealed the notable enhancement of the radiative processes involved in the CDs photoluminescence. The results are included in Table 1 along with the CIE 1931 chromaticity parameters. The most impressive results were recorded in case of D₂O dispersed NHF-CDs where the highest QY (70.97%) was recorded at 350 nm excitation wavelength, value which is more than 2.3x higher compared with the same CDs dispersed in H₂O while at 330 nm excitation the QY is more than 3x higher. For the NHS-CDs the PLQY is almost two times higher when D₂O is used as dispersion medium, a very good value (25.47%) being achieved at 370 nm excitation. In case of the D₂O dispersed Fe-CDs the results are equally impressive the PLQY gain at 330 nm excitation in D₂O medium being almost 2.4x higher (29.10%) compared to the same batch dispersed in H₂O (12.20%). The results recorded for 350 and 370 nm excitation are also notable, 1.63x and 1.9x increased QY values in case of D₂O dispersed Fe-CDs.

The least impressive results were recorded in case of AW-CDs where the highest PLQY (30.17%) was recorded at 370 nm excitation for the batch dispersed in D₂O, only a 1.27x improvement compared with the H₂O dispersion (23.67%). The values recorded at 330 and 350 nm excitation are even less noticeable, the differences between the D₂O and H₂O batches being within 0.3-0.84% range. The CIE 1931 chromaticity parameters revealed in each case minor differences between D₂O and H₂O dispersed CDs results which are in very good agreement with previously discussed configuration of the emission peaks which also revealed insignificant variations between the same batches dispersed in D₂O and H₂O respectively. Overall, the D₂O dispersion medium allows an impressive improvement in terms of efficiency of the CDs specific radiative processes compared with H₂O. The PLQY improvement might vary depending on the specific structural configuration of different types of CDs prepared from a certain precursor. According to our observations, a initially higher PLQY of a certain type of CDs dispersed in H₂O will produce an even higher gain in PL efficiency when D₂O is used. An already good PLQY is most probably due to the richness of the emissive sites within the CDs structure which will highly benefit from a dispersion medium which is less prone to provide non-radiative paths leading to premature deactivation of the excited states.

Table 1. Recorded values for absolute PLQY and CIE 1931 chromaticity parameters.

| | | Absolute PLQY | | |
|---------------------------------|------------------|------------------------|------------------------|------------------------|
| excitation (nm) | | 330 | 350 | 370 |
| CNDs NHF | PLQY (%) | 13.37 | 30.13 | 34.05 |
| <u>H₂O</u> dispersed | abs. error (+/-) | 0.028 | 0.066 | 0.086 |
| | CIE 1931 coord. | x=0.14588 y=0.10874 | x=0.15215 y=0.11844 | x=0.15235 y=0.11802 |
| CNDs NHF | PLQY (%) | 41.48 | 71.27 | 70.97 |
| <u>D₂O</u> dispersed | abs. error (+/-) | 0.086 | 0.143 | 0.146 |
| | CIE 1931 coord. | x=0.15165 y=0.11366 | x=0.15299 y=0.11746 | x=0.15285 y=0.11656 |
| CNDs NHS | PLQY (%) | 11.92 | 12.31 | 12.46 |
| <u>H₂O</u> dispersed | abs. error (+/-) | 0.041 | 0.048 | 0.07 |
| | CIE 1931 coord. | x=0.16148 y=0.14843 | x=0.16749 y=0.17764 | x=0.17203 y=0.20566 |
| CNDs NHS | PLQY (%) | 21.41 | 22.26 | 25.47 |
| <u>D₂O</u> dispersed | abs. error (+/-) | 0.118 | 0.144 | 0.279 |
| | CIE 1931 coord. | x=0.1580 y=0.13088 | x=0.16467 y=0.15574 | x=0.17064 y=0.19365 |
| CNDs Fe doped | PLQY (%) | 12.2 | 10.43 | 5.38 |
| <u>H₂O</u> dispersed | abs. error (+/-) | 0.025 | 0.015 | 0.015 |
| | CIE 1931 coord. | x=0.23316 y=0.55765 | x=0.24067 y=0.6311 | x=0.23791 y=0.58452 |
| CNDs Fe doped | PLQY (%) | 29.1 | 17.09 | 10.29 |
| <u>D₂O</u> dispersed | abs. error (+/-) | 0.086 | 0.021 | 0.057 |
| | CIE 1931 coord. | x=0.23471 y=0.55098 | x=0.23704 y=0.5814 | x=0.23234 y=0.55199 |
| CNDs Argan | PLQY (%) | 15.94 | 19.93 | 23.67 |
| <u>H₂O</u> dispersed | abs. error (+/-) | 0.04 | 0.059 | 0.102 |
| | CIE 1931 coord. | x=0.14839 y=0.08361 | x=0.15448 y=0.10221 | x=0.15723 y=0.12234 |
| CNDs Argan | PLQY (%) | 16.24 | 21.77 | 30.17 |
| <u>D₂O</u> dispersed | abs. error (+/-) | 0.04 | 0.069 | 0.164 |
| | CIE 1931 coord. | x=0.15136 y=0.09372 | x=0.15611 y=0.11137 | x=0.15501 y=0.1093 |

3.1.3. Fluorescence lifetime (LT) measurements

In Figure 6a-h are illustrated the typical time-resolved fluorescence decay profiles (in Figure S1a-h the residuals of the fluorescence decay fitting), while in Table 2 are presented the relevant decay characteristics. To accurately model the fluorescence decay behavior, we employed a single exponential decay model or a multi-exponential decay model, depending on the sample behavior (eq. 1) [9,27,28]:

$$I(t) = \sum_{i=1}^n a_i \cdot \exp\left(\frac{-t}{\tau_i}\right) \quad (1)$$

where $I(t)$ is the fluorescence intensity, a_i corresponds to the amplitude of each component i , which reflects the relative contribution of that specific decay process. Each component is characterized by a unique fluorescence lifetime τ_i , and the sum of all amplitudes is normalized to 1 ($\sum a_i = 1$), ensuring that the model represents the entirety of the observed decay. To further understand the contribution of each lifetime component, we calculated the fractional concentration, (f_i), of each decay time, which quantifies the proportion of fluorescence attributable to each lifetime (eq. 2):

$$f_i = \frac{a_i \tau_i}{\sum_{j=1}^n a_j \tau_j} \quad (2)$$

The sum of f_i values is also normalized to 1 ($\sum_{i=1}^n f_i = 1$), indicating that the calculated fractions account for the total observed fluorescence. The average lifetime ($\langle\tau\rangle$) was given by the equation(2):

$$\langle\tau\rangle = f_1\tau_1 + f_2\tau_2 + f_3\tau_3 \quad , \quad (3)$$

In the present study, the fluorescence decay in water was best described by a three-exponential model. However, the same three-exponential model also applied to two of the deuterated samples, NHS-CDs and AW-CDs. Interestingly, for the NHF-CDs and Fe-CDs samples in deuterated solvent, a single-exponential decay was observed. Additionally, we found that the D₂O dispersion medium increased the average lifetimes compared to the H₂O dispersed samples, a phenomenon reported by others in the literature as well [9,28].

Additionally, to provide insight into the decay mechanisms, we derived both radiative (k_r) and non-radiative (k_{nr}) decay constants (Table 2) from nanosecond lifetime measurements and quantum yields using the following equations (2):

$$k_r = \frac{\Phi}{\langle\tau\rangle} \quad , \quad (4)$$

$$k_{nr} = \frac{1 - \Phi}{\langle\tau\rangle} \quad , \quad (5)$$

Generally, k_{nr} is higher than k_r for each sample, indicating that non-radiative decay processes are more prominent, which may contribute to the observed differences in fluorescence behavior in H₂O and D₂O. Furthermore, the influence of the deuterated solvent led to a decrease in the non-radiative decay constant (k_{nr}) and an increase in the radiative decay constant (k_r). This shift in decay pathways aligns with the observed increase in quantum yield when the samples are dispersed in deuterated solvent compared to regular water.

Table 2. Absolute PLQY at $\lambda_{ex} = 370$ nm, radiative and non-radiative decay rate constants, and fluorescence lifetimes of the analyzed samples.

| Sample code | Φ (%) | k_r^* (ns ⁻¹) | k_{nr}^* (ns ⁻¹) | τ_1 (ns) | a_1 (%) | f_1 | τ_2 (ns) | a_2 (%) | f_2 | τ_3 (ns) | a_3 (%) | f_3 | χ^2 | $\langle\tau\rangle$ (ns) |
|---------------------------------------|------------|-----------------------------|--------------------------------|---------------|-----------|-------|---------------|-----------|-------|---------------|-----------|-------|----------|---------------------------|
| NHF-CDs H ₂ O dispersed | 34,05 | 0,042 | 0,082 | 8,38 | 81,43 | 0,952 | 2,09 | 16,33 | 0,048 | 0,11 | 2,24 | 0,000 | 1,04 | 8,07 |
| NHF-CDs D ₂ O dispersed | 70,97 | 0,086 | 0,035 | 8,22 | 100,00 | 1,000 | - | - | - | - | - | - | 1,09 | 8,22 |
| NHS-CDs H ₂ O dispersed | 12,46 | 0,014 | 0,101 | 10,68 | 44,22 | 0,698 | 4,20 | 46,42 | 0,289 | 0,95 | 9,36 | 0,013 | 1,11 | 8,68 |
| NHS-CDs D ₂ O dispersed | 25,47 | 0,024 | 0,071 | 12,72 | 47,40 | 0,744 | 4,39 | 45,47 | 0,246 | 1,04 | 7,13 | 0,009 | 1,13 | 10,56 |
| NHS-CDs H ₂ O dispersed | 5,38 | 0,005 | 0,089 | 12,98 | 17,83 | 0,222 | 9,99 | 81,00 | 0,778 | 0,09 | 1,17 | 0,000 | 1,10 | 10,66 |
| Fe-CDs D ₂ O dispersed | 10,29 | 0,007 | 0,061 | 14,65 | 100,00 | 1,000 | - | - | - | - | - | - | 1,07 | 14,65 |
| AW-CDs H ₂ O dispersed | 23,67 | 0,029 | 0,094 | 9,85 | 46,75 | 0,673 | 4,49 | 49,43 | 0,324 | 0,47 | 3,82 | 0,003 | 1,11 | 8,09 |
| AW-CDs D ₂ O dispersed | 30,17 | 0,028 | 0,066 | 12,88 | 47,32 | 0,713 | 5,09 | 46,97 | 0,280 | 1,12 | 5,17 | 0,007 | 1,14 | 10,62 |

Φ = fluorescence quantum yield, $\tau_{1,2,3}$ = fluorescence lifetimes, $a_{1,2,3}$ = amplitude of the components, $f_{1,2,3}$ = fractional concentrations, $\langle\tau\rangle$ = average fluorescence lifetimes, k_r = radiative rate constants, k_{nr} = non-radiative rate constants

*calculated for the Φ at $\lambda_{ex} = 370$ nm

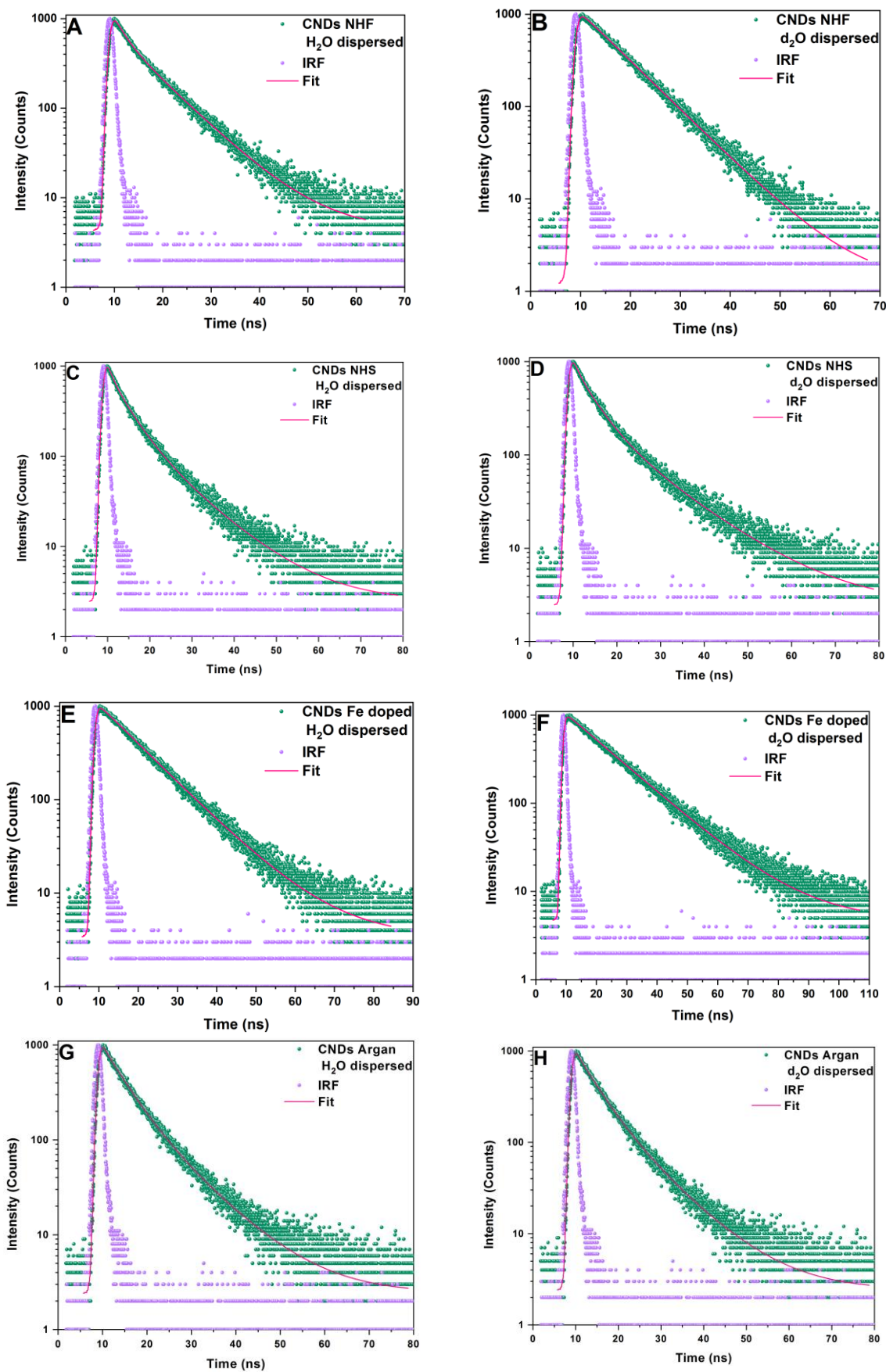


Figure 6. The typical time-resolved fluorescence decay profiles of the (a) NHF-CDs/H₂O, (b) NHF-CDs D₂O, (c) NHS-CDs/H₂O, (d) NHS-CDs/D₂O, (e) Fe-CDs/H₂O, (f) Fe-CDs/D₂O, (g) AW-CDs/H₂O, (h) AW-CDs/D₂O samples.

The reduction in k_{nr} suggests that the non-radiative relaxation processes, such as vibrational relaxation and other energy-dissipating mechanisms, are less prominent in deuterated solvent. This reduction could be attributed to the isotope effect, where deuterium atoms, with their greater mass, decrease vibrational energy dissipation, effectively reducing non-radiative losses. At the same time, the increase in k_r indicates that the radiative decay pathway (fluorescence emission) becomes more favorable in the presence of deuterated solvent, contributing to the enhanced quantum yield. These changes suggest that deuterated solvents can shift the balance between radiative and non-radiative decay processes, enhancing fluorescence efficiency by promoting radiative decay while suppressing non-radiative pathways [29]. Therefore, the LT investigation results are in very good agreement with PLQY and Steady State fluorescence investigations, sustaining very well our opinion that the "isotope effect" induced by the D₂O presence play an indirect role in enhancing the PL emission by providing a more favorable environment for the radiative transitions.

3.2. Characterization of the D₂O dispersed CDs

As stated above, the experimental procedure for the preparation of each type of investigated CDs was kept unchanged as detailed in our previous reported works [14-17] where in-depth morpho-structural investigation was performed and discussed. Since the only difference consist in the final dispersion medium (D₂O) the investigations presented in this work were focused on the morphological aspects which could provide new information. Therefore DLS (dimensional analysis) was performed for each type of CDs dispersed in D₂O.

3.2.1. Dimensional (DLS) investigation

Freshly prepared samples of each type of CDs dispersed in D₂O were investigated. Also, for the evaluation of long-term stability of the dispersions, same samples were investigated again after 1 week. In Figure 7 (a-d) are presented the dimensional distributions for each type of CDs dispersed in D₂O, freshly prepared and after 1 week of aging.

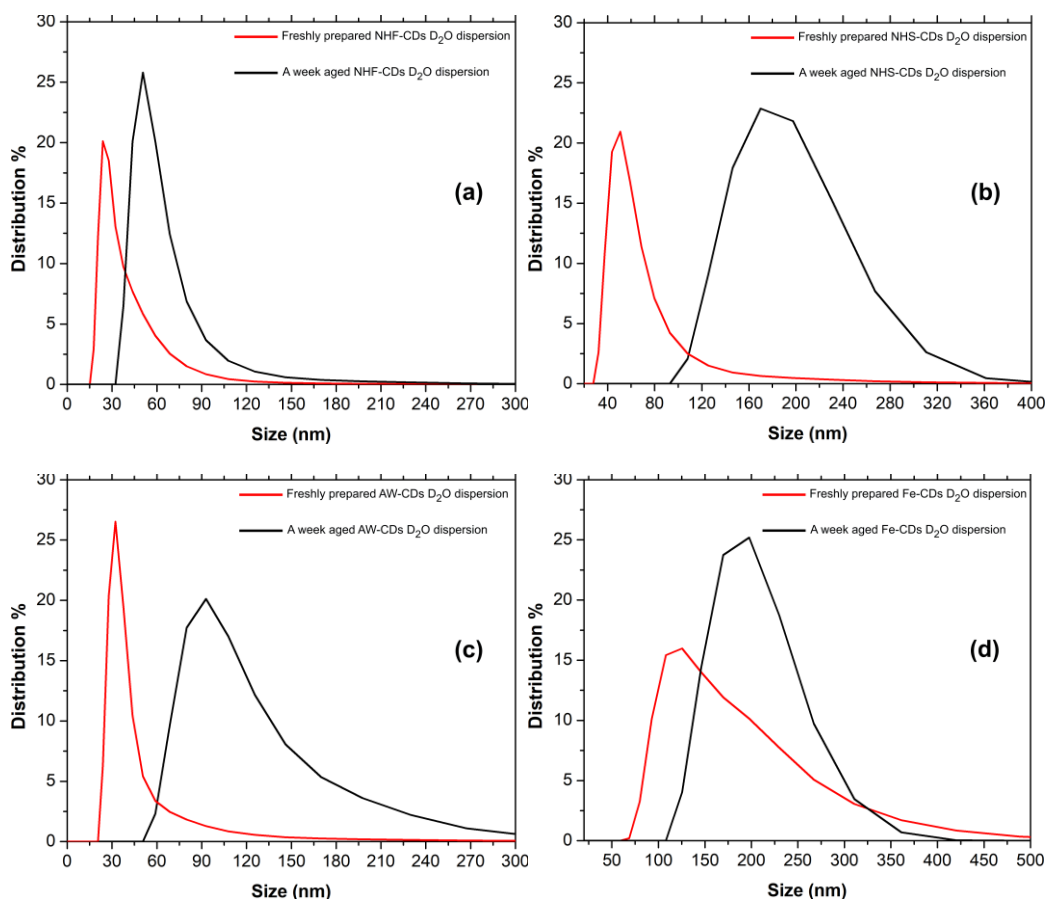


Figure 7. Dimensional distribution of freshly prepared/1 week aged of (a) NHF-CDs, (b) NHS-CDs, (c) AW-CDs and (d) Fe-CDs dispersed in D₂O

All the prepared samples present, as expected, an agglomeration tendency which was observed irrespective of the type of solvent used as dispersion medium. The freshly prepared NHF-CDs/D₂O dispersion size distribution is mainly situated within 30-90 nm range. As demonstrated in our previous works, CDs present a clusterization tendency which became even more noticeable in case of the aged dispersion where the size distribution migrates within 40-140 nm range. In case of NHS-CDs, freshly prepared dispersion

presents a narrower size distribution (40-120 nm) compared with the aged dispersion where a broad 120-320 nm distribution was observed most probably due to an even more clusterization tendency. This behavior is almost the same in case of AW-CDs where the freshly prepared dispersion presents a narrow distribution (25-90 nm) which became significantly broader for the aged dispersion (60-250 nm). The Fe-CDs/D₂O dispersion behave differently compared with the rest of the investigated samples, with an initial broad distribution (60-400 nm) which remain also large but slightly translated to higher dimensional range (100-400 nm). This particular behavior could be a result of iron presence within the CDs structure. Overall, the stability of the dispersions is slightly better compared with the same CDs types but dispersed in water.

Interestingly, in case of NHF-CDs, AW-CDs and Fe-CDs dispersions the PL intensity remained unchanged after 1 week, no notable differences being noticed both visual and instrumental which might additionally sustain the key role of the dispersion medium in achieving a better emissive intensity. The aged NHS-CDs/D₂O dispersion presents a slightly fainter emission intensity. Compared with samples of same CDs type dispersed in water, the PL emission is markedly better preserved.

4. Conclusions

The photoluminescence (PL) properties of several types of Carbon Dots (CDs) dispersed in deuterium oxide were thoroughly investigated. Through simple replacement of the commonly used aqueous dispersion medium with D₂O, the CDs prepared from various precursors are able to achieve an impressive enhancement of their PL emission intensity. In the present work four types of CDs were prepared, in each case the emission intensity being markedly enhanced. The recorded PL quantum yield (QY) was found to increase at least 1.27x to 2.3x compared with the same CDs batches dispersed in H₂O, in the most favorable case an impressive 70.97% QY being achieved. The isotope effect over the PL properties of fluorophores (including CDs) is a less investigated research topic with relatively scarce reported works. Unlike many of the reported studies which hypothesize that the observed PL intensity enhancement is a result of the isotope effect induced by spontaneous H → D exchange. within the CDs structure, our investigation rather supports an alternative mechanism where the isotope effect might be indirectly involved. In our view, by switching H₂O to D₂O as dispersion medium is able to provide a more favorable environment which diminishes the non-radiative deactivation paths thus favoring the radiative relaxations through photon production. Given the particularities of D₂O which dissociates less than H₂O and the new vibrational conditions due to the presence of the heavier deuterium in the surroundings of the emissive sites provides a better environment for the photonic processes within the CDs.

Supplementary Materials: The following supporting information can be downloaded at: www.mdpi.com/xxx/s1, Figure S1: Recorded Lifetime residuals.

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Supplementary Information

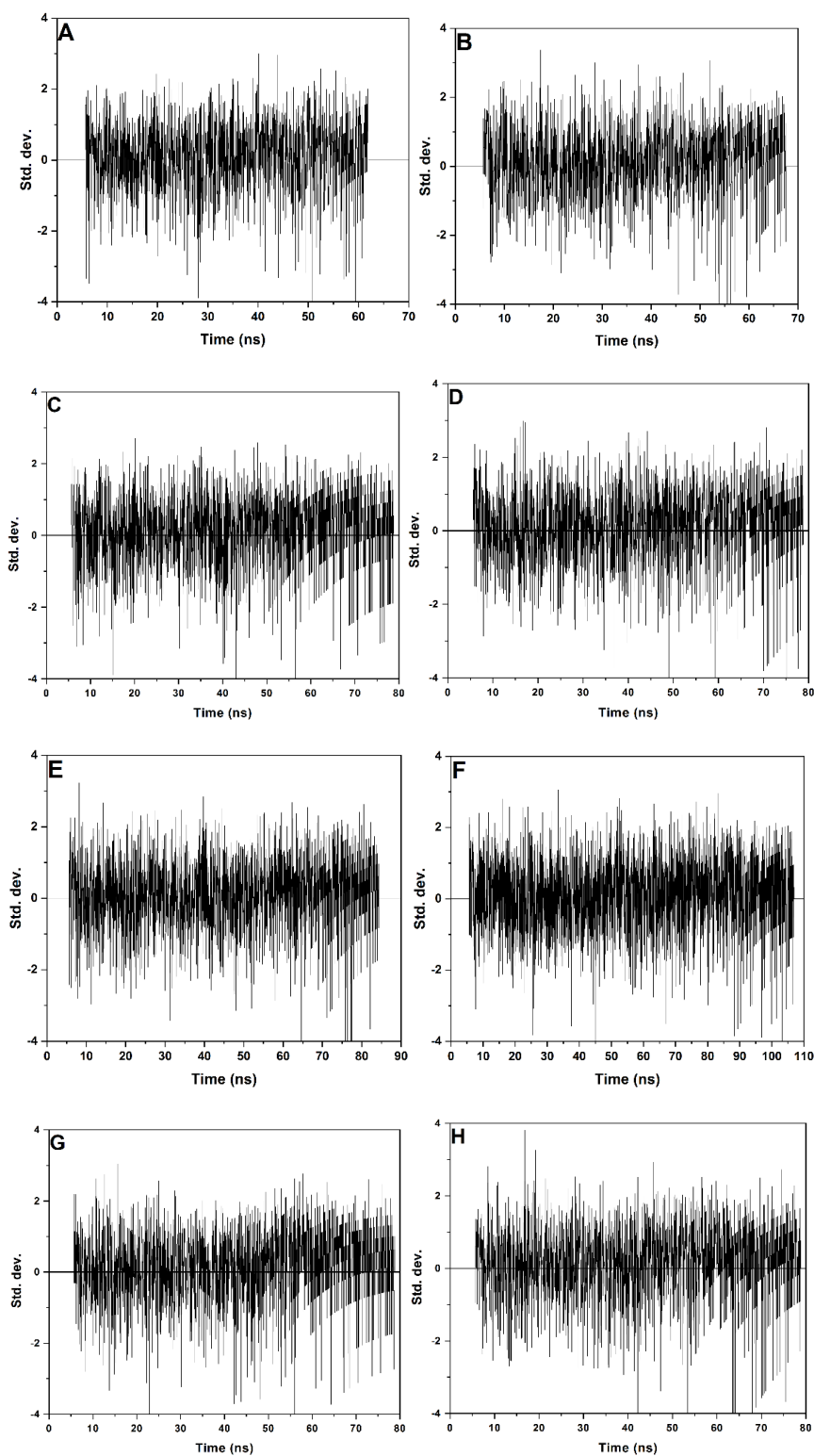


Figure S1. Time-resolved fluorescence (LT) decay residuals profiles of the (a) NHF-CDs/H₂O, (b) NHF-CDs D₂O, (c) NHS-CDs/H₂O, (d) NHS-CDs/D₂O, (e) Fe-CDs/H₂O, (f) Fe-CDs/D₂O, (g) AW-CDs/H₂O, (h) AW-CDs/D₂O samples.