Determination of Fe$^{3+}$ upon Special “Upconversion Luminescence” of Dopamine

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Supporting Information

ABSTRACT: A promising technique based on the luminescence with long wavelength excitation and short wavelength emission (LExL, $\lambda_{\text{ex}} > \lambda_{\text{em}}$) is developed. This LExL is different from traditional upconversion luminescence (UCL). The LExL, namely, special “UCL”, is realized by a xenon light source of a common spectrophuorometer. In this work, we found that dopamine (DA) has this LExL phenomenon. The LExL of DA is mainly caused by the excitations of second-order diffraction light ($\lambda_{\text{ex}}/2$). The two-photon absorption properties of DA have been calculated employing the density functional response theory. The LExL and Stokes luminescence (SL, $\lambda_{\text{ex}} < \lambda_{\text{em}}$) of DA both showed static quenching upon the addition of Fe$^{3+}$. Dual-mode luminescence methods upon LExL ($\lambda_{\text{ex}}/\lambda_{\text{em}}$ at 565/317 nm) and SL ($\lambda_{\text{ex}}/\lambda_{\text{em}}$ at 282/317 nm) of DA were applied for the selective determination of Fe$^{3+}$. The detection limits are 0.30 and 0.52 $\mu$mol L$^{-1}$ for LExL and SL, respectively. In addition, their linear ranges for Fe$^{3+}$ determination are both from 0.70 to 30 $\mu$mol L$^{-1}$. The LExL method of DA not only meets the basic determination criteria for Fe$^{3+}$ but also offers additional advantages in resisting more interferences and shows satisfactory feasibility performances.

1. INTRODUCTION

Iron, an important trace element in human body, is indispensable on the cell metabolism, enzyme catalysis, and cytotoxicity. However, iron overload can break the iron balance in the body and cause adverse consequences. The massive discharge of iron-rich industrial wastewater aggravates environmental pollution and health problems. Dopamine (DA, 3,4-dihydroxyphenethylamine) is closely related to the normal operation of cardiovascular and hormonal systems in mammalian animals. Some research results have showed that the interaction between iron ions and DA/DA-derived neuromelamins highly connect with neurodegenerative diseases. Therefore, the interaction of Fe$^{3+}$ with DA and the precise determination of Fe$^{3+}$ is of crucial important. Heretofore, many polydopamine (PDA)- and DA-functionalized materials were as excellent sensors for detection of Fe$^{3+}$. However, these PDA–DA-functionalized materials undergo complicated and time-consuming modifying processes. Furthermore, excitation wavelengths of these fluorescent sensors are mostly located in the ultraviolet region. As we know, ultraviolet radiation can cause a certain degree of light damage. Therefore, it is necessary to develop a longer wavelength excited luminescent method to determine Fe$^{3+}$ and study direct interaction between DA and Fe$^{3+}$. Generally, upconversion luminescence (UCL) refers to the luminescence of emission wavelength shorter than excitation wavelength. UCL has been widely applicable in biosensing, phototherapy, drug delivery, and so forth. A laser is usually required as a light source to achieve two- and multi-photon excitation. However, Lee et al. has developed a special “UCL” technique achieved by a xenon light source on the common spectrophuorometer, which is also a luminescence method based on the excitation wavelength longer than the emission wavelength (LExL, $\lambda_{\text{ex}} > \lambda_{\text{em}}$). Usually, the excitation wavelength of the special “UCL” is located at double that of Stokes luminescence (SL, $\lambda_{\text{ex}} < \lambda_{\text{em}}$), that is $\lambda_{\text{ex}} = 2\lambda_{\text{em}}$. Although the mechanism of the luminescence is controversial, the special “UCL” technique can be effectively applicable in spectral characterization and the quantitative determination of target analytes. Salinas-Castillo’s team has made use of the special “UCL” and down-conversion fluorescent properties of their carbon dots for selective detection of Cu$^{2+}$ ion. In addition, the special “UCL” method shows an obvious advantage in eliminating interference caused by Fe$^{3+}$. Zhang et al. constructed a nanoprobe [nitrogen-doped carbon dots/gold nanoparticles (NC-dots/AuNPs)] to selectively detect cysteine with multiple signals: colorimetric, photoluminescence ($\lambda_{\text{ex}}/\lambda_{\text{em}}$ at 400/475 nm), and special “UCL” ($\lambda_{\text{ex}}/\lambda_{\text{em}}$ at 800/490 nm). However, so far, a limited number of LExL/special “UCL” methods were provided the author and source are cited.

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reported and focused on the graphene/carbon-based quantum dots. The exploration of the LExL/special “UCL” technology needs to be further studied.

In this work, we found the LExL phenomenon also exists in the organic small molecule (DA). In addition, we studied the luminescence mechanism by the fluorescence experiments and time-dependent density functional theory (DFT). The LExL of DA is mainly caused by the excitations of second-order diffraction light ($\lambda_{exL}/2$). The LExL and SL of DA could both be used in studying the fluorescence quenching effect of DA by $\text{Fe}^{3+}$. The schematic diagram of interaction mechanism of DA with $\text{Fe}^{3+}$ is shown in Scheme 1. The dual-mode “turn-off” luminescence methods upon the LExL and SL of DA can be applied to the selective detection of $\text{Fe}^{3+}$. The two methods confirmed the feasibility in the determination of $\text{Fe}^{3+}$ in the actual water samples. In addition, the LExL method shows better linear correlation, test stability, and the lower detection limit.

2. RESULTS AND DISCUSSION

2.1. Spectral Properties of DA. Fluorescence information of DA could be obtained by 3D fluorescence spectra (Figure 1). The excitation peaks of SL are at 220 and 282 nm (Figure 1A). Surprisingly, we found that DA also has LExL properties. Corresponding excitation wavelengths of LExL are 383, 446, and 565 nm, respectively (Figure 1B). In addition, emission peak positions are all the same at 317 nm.

Both the LExL and SL of DA show excitation-independent luminescent properties (Figure S1). In addition, under excitation at 565 and 446 nm for LExL and 282 and 220 nm for SL and the strongest fluorescence emission at 317 nm are obtained. The excitation wavelengths of LExL are located at about twofold that of SL. The phenomena indicate that LExL of DA contains the luminescence by the excitation of second-order diffraction light (565/2 nm, 446/2 nm).

Some reports attributed the special “UCL” ($\lambda_{exL}/2$) of graphene/carbon-based quantum dots to the multiphoton active process from their own structures. Although these explanations are not completely sufficient, one can realize that this special “UCL” arises from the structures of fluorophores. In view of this point, we speculate that the LExL of DA may be related to its two-photon absorption (TPA) characteristic. TPA cross sections ($\sigma_{TPA}$) can be used in estimating the ability of the fluorophores absorbing two photons. To explore the possibility, we calculated TPA properties of DA by response theory at the default time-dependent DFT level at the B3LYP and CAM-B3LYP functional with the 6-31G(d) basis set in Dalton 2013 package. In this work, the pH of DA solution is about 5.50, and the protonated DA state is more reasonable (DA, $pK_{a1} = 9.0$). Theoretical calculation results (optimized conformers, TPA properties, etc.) of protonated DA are shown in the Supporting Information. The lowest energy conformers of protonated DA are illustrated in Scheme S1. Its wavelengths of bigger $\sigma_{TPA}$ are at 446, 383, and 353 nm as obtained by B3LYP functional and at 424, 367, and 317 nm as calculated by CAM-B3LYP functional, respectively.

To verify that the LExL excited by 565 nm light is not entirely the excitation of second-order diffraction light ($\lambda_{exL}/2$), we put a 500 nm longpass filter in the excitation channel (Figure S2). Although most LExL of DA was eliminated, there is still a weak emission peak at about 310 nm. The results indicate that besides the excitation of second-order diffraction light ($\lambda_{exL}/2$: 565/2 nm, 446/2 nm, 383/2 nm), the LExL of DA ($\lambda_{exL}$ at 565, 446, and 383 nm) may be caused by other luminescence.

The influence of the pH on the fluorescence of DA was studied. The 565 nm is selected as the excitation wavelength of LExL for further researches because of the relatively lower excitation energy and stronger fluorescence intensities than excited by 383 nm or 446 nm lights. Correspondingly, the excitation wavelength of SL is chosen to be 282 nm. We measured the intensities of LExL and SL of DA under different pH conditions. The results are shown in Figure 2A. The fluorescence intensities of LExL and SL of DA at 317 nm both display pH-dependent properties. That is, the fluorescent intensities of DA are high and nearly constant when pH < 5.0, while the intensities are relatively weak at pH 10 or higher. In addition, the emission intensity of DA decreases linearly within the pH range of 5.0−10.0. The pH-dependent performance of LExL and SL of DA may be due to the protonation or deprotonation and the oxidation of DA and formation of PDA. To verify this point, the UV−vis spectra of DA under different pH were investigated (Figure 2B). The absorption peaks of DA at 280 nm are assigned to the $\pi-\pi^*$ transition of sp$^2$ domains in aromatic ring of DA. As the pH value increases from 2.0 to 5.0, the absorbance of DA is decreased (Figure 2B, inset). Oppositely, in this pH range, the strongest fluorescence emission of DA is obtained (Figure 2A), which indicates that low pH or higher protonation is favorable for the luminescence of DA. However, along with the increase of pH value in the range of 6.0−8.0, the absorption peaks show a gradual bathochromic-shift from 280 to 286 nm and the absorbencies rise, which are attributed to the different degree of deprotonation of DA. When the pH value is larger than 10, the absorption peaks of DA at 280 nm show significant red shift.
The concentration of Fe\(^{3+}\) were monitored (Figure 3A, B). The spectr ao ft hE x La nD S Lo fD Ai int h ev a ri o u s Fe\(^{3+}\) concentrations from 0.7 to 100. The pH values decrease from 5.54 to 4.50 with the increase of this pH range, the intensities of LExL and SL of DA are both obvious quenching eff ects of the LExL and SL of DA are both obtained after the addition of Fe\(^{3+}\). In view of the pH effect on the luminescence properties of DA, the pH of DA solution containing various concentrations of Fe\(^{3+}\) were also measured. The pH values decrease from 5.54 to 4.50 with the increase of Fe\(^{3+}\) concentrations from 0.7 to 100 \(\mu\)mol L\(^{-1}\). However, in this pH range, the intensities of LExL and SL of DA are both the maximum value and almost remained unchanged (Figure 2A). Therefore, the quenching effects of LExL and SL should be induced by the interaction of DA with Fe\(^{3+}\) rather than pH. Generally, static and dynamic quenching is differentiated depending on the change in fluorescence quenching efficiency at different temperatures.\(^{30}\) According to the Stern–Volmer equation: \(I_0/I = 1 + K_{Q}[Q]\), the quenching curves of LExL and SL of the system are plotted at different temperatures of 288, 298, and 308 K (Figure S3). Here, \(I_0\) and \(I\) are the fluorescence intensities of DA in the absence and presence of quencher (Fe\(^{3+}\)), respectively. \(K_Q\) is the quenching constant. \([Q]\) is the concentration of quencher (Fe\(^{3+}\)). The linear plots suggest a sole static or dynamic quenching.\(^{30}\) In addition, the corresponding quenching parameters of the system are showed in Table S1. The quenching constants for SL and LExL of DA were 3.56 \(\times\) 10\(^8\) and 3.48 \(\times\) 10\(^8\) L mol\(^{-1}\) at 288 K, 2.43 \(\times\) 10\(^8\) and 2.38 \(\times\) 10\(^8\) L mol\(^{-1}\) at 298 K, and 2.10 \(\times\) 10\(^8\) and 1.97 \(\times\) 10\(^8\) L mol\(^{-1}\) at 308 K, respectively. With increasing temperature, the quenching constants show apparent decreases. Therefore, it can be speculated that there is a static quenching process when Fe\(^{3+}\) interacts with DA.

To further verify the quenching mechanism, the fluorescence decay curves were recorded at 280 nm excitation.

The fluorescence lifetimes were obtained by using the single exponential fitting (Figure S4). The lifetimes of DA and DA–Fe\(^{3+}\) complexes are calculated to be 0.84 ns (\(\chi^2 = 0.909\)) and 0.78 ns (\(\chi^2 = 1.014\)), respectively. Their fluorescence lifetimes are almost unchanged, which also further demonstrate that the fluorescence quenching of DA caused by Fe\(^{3+}\) is a static quenching process.\(^{11}\)

2.3. Interaction of DA with Fe\(^{3+}\). To explore the interaction between DA and Fe\(^{3+}\), the absorption spectra of DA in the presence of various concentrations of Fe\(^{3+}\) were investigated (Figure 4). Water is selected as the reference solution. Inset of Figure 4 shows that the absorption band of Fe\(^{3+}\) has some overlapping with that of DA, but the absorbance at 280 nm of DA–Fe\(^{3+}\) is not the simple superposition of that of Fe\(^{3+}\) and DA, suggesting that the interaction exists between DA and Fe\(^{3+}\). The absorption profiles of the DA–Fe\(^{3+}\) system are somewhat similar to those of DA at different pH (see Figure 2B). Differently, a shoulder peak of 310 nm gradually grows upon adding of Fe\(^{3+}\) until it merges with the peak of 280 nm. The change of the absorption peak may be attributed to the covalent conjugating between Fe\(^{3+}\) with catechol group of...
DA. In addition, the oxidation of DA can also lead to the emergence of absorption peak in ultraviolet region. Thus, we believe that the absorption at 310 nm may be partly the result of the oxidation of DA induced by Fe$^{3+}$. The broad absorption band of the DA–Fe$^{3+}$ system appearing around 380–600 nm partly overlaps with the 400–600 nm absorption band of DA at high pH (Figure 2B). In addition, the maximum peak position of the DA–Fe$^{3+}$ is at about 470 nm, distinguishing it from that of DA at 440 nm in high pH condition. In addition, the absorption peak of PDA–Fe$^{3+}$ is around 490 nm. Therefore, the broad absorption peak of 380–600 nm is presumably attributed to the formation of PDA–Fe$^{3+}$ complexes.

We monitored the Fourier transform infrared (FT-IR) spectra of DA and DA–Fe$^{3+}$ to obtain the combination information of DA–Fe$^{3+}$ complexes (see Figure S5). The feature peaks of DA disappeared after reacting with Fe$^{3+}$, including 1504 cm$^{-1}$ (NH$_2$ scissoring vibration), 1341 cm$^{-1}$ (CH$_2$ bending vibration), 1322 cm$^{-1}$ (C–O–H bending vibration), and 1187 cm$^{-1}$ (C–O symmetry vibration). The peak of DA–Fe$^{3+}$ around 1634 cm$^{-1}$ widened compared with that of DA, indicating the existence of C=C=C stretching vibration assigned to the indole derivatives. These results all verified the oxidation and intramolecular cyclization of DA and the subsequent formations of PDA–Fe$^{3+}$.

To get further insights into the interaction of DA and Fe$^{3+}$, we added the strong chelating agent ethylenediaminetetraacetic acid (EDTA) to the DA–Fe$^{3+}$ system. As shown in Figure S6, EDTA has little effect on the fluorescence properties of the LExL and SL of DA. However, the fluorescence of the DA–Fe$^{3+}$ system is regenerated after adding EDTA. The fluorescence recovery indicates that the chelation between EDTA and Fe$^{3+}$ weakens the interaction of Fe$^{3+}$ with DA and induces the dissociation of Fe$^{3+}$ from DA.

Another interesting phenomenon is noted in the cyclic processes of adding Fe$^{3+}$ and EDTA into the DA (Figure S5).

![Figure 5](image-url)  
**Figure 5.** Reversible switching of LExL ($\lambda_{ex}$= 565 nm, blue) and SL ($\lambda_{ex}$ at 282 nm, black) of DA (10 μmol L$^{-1}$) at 317 nm between the ON and OFF states with the alternate addition of 30 μmol L$^{-1}$ Fe$^{3+}$ and 50 μmol L$^{-1}$ EDTA.

The alternative addition of Fe$^{3+}$ and EDTA enabled the fluorescence intensity of DA at 317 nm to alternate between on and off states several times. At first, the addition of EDTA into the DA–Fe$^{3+}$ solution led to about 74% recovery rate of the fluorescence. The incomplete recovery in the fluorescence intensity indicates there are some changes in the existence forms of DA after the reaction with Fe$^{3+}$. Then, the quenching effect caused by Fe$^{3+}$ and the fluorescence recoveries by EDTA on LExL and SL of DA both become gradually weaker. After several cycles, the addition of EDTA has little influence on the fluorescence intensities of the system. The reason may lie in that DA gradually becomes into other forms induced by Fe$^{3+}$. According to the FT-IR, UV spectra analysis, the multiple interaction modes between DA and Fe$^{3+}$ may include the complexation of DA with Fe$^{3+}$, oxidation of DA, and gradual formations of PDA–Fe$^{3+}$. The chelation between EDTA and Fe$^{3+}$ can induce the dissociation of Fe$^{3+}$ from DA and weaken the complexation of Fe$^{3+}$ with DA; thus, the partial fluorescence of DA is restored. After several cycles, DA partially oxidizes and polymerizes into PDA (Figure S6, gray curve), and finally EDTA cannot restore the fluorescence of residual DA (Figure S6, magenta curve). The specific reaction processes need to be studied in detail in the future.

**2.4. Detection of Fe$^{3+}$:** Here, 10 μmol L$^{-1}$ DA is chosen for Fe$^{3+}$ detection. In this case, DA has an appropriate fluorescence intensity. The intensities of LExL and SL both show the strongest quenching within 3 min after adding Fe$^{3+}$ to DA solution (Figure S7). As shown in Figure 6A,B, there are good linear correlations between $(I_0 - I)/I_0$ and Fe$^{3+}$ concentration ranging from 0.70 to 30 μmol L$^{-1}$ for LExL ($R^2 = 0.9983$) and SL ($R^2 = 0.9833$). The limits of detection (LODs) are 0.30 and 0.52 μmol L$^{-1}$ for LExL and SL, respectively. LOD was calculated according to 3S/N, where S represents the standard deviation of 11 measurements of 10 μmol L$^{-1}$ DA and N is the slope of the calibration curve. The linear correlation and detection limit of the LExL-based method are superior to those of the SL-based method. The LODs of two methods are both lower than the maximum permitted Fe$^{3+}$ content (5.4 μmol L$^{-1}$) in drinking water of state standard. And what is more, compared with some methods (Table S2), our strategies could avoid undergoing complicated and time-consuming modifying processes. However, the sensitivity of the proposed method needs to be further improved.

**2.5. Selectivity and Interference Study:** To evaluate the anti-interference ability and selectivity of the proposed...
methods, the response signals of the LExL and SL of DA to a variety of metal cations without Fe$^{3+}$ and the mixture of Fe$^{3+}$ with other various metal ions were monitored (Figure 7). Al$^{3+}$, in all tested ions except for Fe$^{3+}$, is the other one with a more distinguishable quenching effect on the luminescence signal of DA. The results may be attributed to the high affinity of DA for trivalent metal ions. However, the quenching efficiency of Al$^{3+}$ is only about a quarter of that of Fe$^{3+}$, which indicates that the charge density of metal ions is not really the main cause of the quenching process in this work. In addition, the fluorescence intensity changes of DA caused by other tested metal ions are less than 10 percent. In addition, the mixture of various metal ions has little inhibition to the fluorescence quenching of DA induced by Fe$^{3+}$. These results illustrate that the dual-mode DB-based fluorescence method possesses high selectivity for the detection of Fe$^{3+}$. Furthermore, Ca$^{2+}$, Cu$^{2+}$, Hg$^{2+}$, Al$^{3+}$, Ba$^{2+}$, Mg$^{2+}$, Zn$^{2+}$, Pb$^{2+}$, Cd$^{2+}$, Ni$^{2+}$, and Fe$^{3+}$ ion have similar enhancement or quenching effect on LExL and SL of DA. However, Pb$^{2+}$ and Cd$^{2+}$ ions have higher fluorescence enhancements for SL than LExL of DA. Additionally, Ag$^+$, K$^+$, Na$^+$, Mn$^{2+}$, and Co$^{2+}$ ions can enhance the intensities of the SL of DA and, alternatively, reduce those of the LExL of DA. The changes in their intensity of the SL are bigger than those of the LExL. Therefore, LExL of DA may be a better choice when Fe$^{3+}$ coexists with Pb$^{2+}$, Cd$^{2+}$, Ag$^+$, K$^+$, Na$^+$, Mn$^{2+}$, or Co$^{2+}$ ions.

2.6. Performance in Real Samples Analysis. To demonstrate the feasibility of the dual-mode luminescence of DA for the Fe$^{3+}$ detection, the standard addition method was employed for testing. In addition, the recovery experiments of Fe$^{3+}$ were carried out in the actual water samples of Daming Lake water (pH = 7.04) and tap water (pH = 6.89) samples in Jinan of Shandong Province. The pH of the spiked samples of Daming Lake water and tap water samples are in the range of 6.86–6.88 and 6.75–6.79, respectively. During the changes of pH values within 0.20, in this pH range, the intensities of LExL and SL of DA are almost unchanged (Figure 2A); thus, we can exclude the influence of pH change on sample determination. The detection results are summarized in Table S3. The recoveries of 89.1–106.0% are obtained for Daming Lake water. For the tap water sample, the recovery rates are between 90.6 and 108.2%. Meanwhile, the contents of Fe$^{3+}$ in the tap water sample monitored by the LExL and SL of DA are approximately the same. The relative standard deviations of LExL (0.19–5.0%) are almost lower than those of SL (0.50–8.3%) in the same measurement, indicating a better test stability of LExL. These results demonstrate that the dual-mode luminescence of DA exhibits cheerful prospects in practical application for monitoring Fe$^{3+}$.

3. CONCLUSIONS

In summary, we studied the luminescence characteristic of LExL of DA through fluorescence measurements using a common spectrophotometer with a xenon-lamp light source and the calculation employing the density functional response theory. The LExL of DA is mainly caused by the excitations of second-order diffraction light ($\lambda_{ex}/\lambda_{em}$). The dual-mode luminescence methods based on LExL and SL of DA were adopted for studying the interaction of DA with Fe$^{3+}$ and the selective determination of Fe$^{3+}$. The proposed two methods for the detection of Fe$^{3+}$ are quick (2–3 min) and simple in design without complex synthesis processes, and the results of dual signal responses are more reliable. The LExL method is proved to be a sensitive and selective method for the determination of Fe$^{3+}$. Comparing with SL method, the LExL method can resist more interferences. The method may be a better choice when Fe$^{3+}$ coexists with Pb$^{2+}$, Cd$^{2+}$, Ag$^+$, K$^+$, Na$^+$, Mn$^{2+}$, and Co$^{2+}$ ions. In addition, the LExL of DA shows better linear correlation, test stability, and lower detection limit. We hope that the LExL/special “UCL” method enables promising applications in spectral characterization and the quantitative determination of target analytes.

4. EXPERIMENTAL SECTION

4.1. Materials and Reagents. Dopamine hydrochloride was commercially obtained from National Institutes for Food and Drug Control (Beijing, China). Metal cations of Fe$^{3+}$, Na$^+$, K$^+$, Ag$^+$, Hg$^{2+}$, Cd$^{2+}$, Cu$^{2+}$, Zn$^{2+}$, Mn$^{2+}$, Ba$^{2+}$, Pb$^{2+}$, Ni$^{2+}$, Mg$^{2+}$, Ca$^{2+}$, Pb$^{2+}$, Al$^{3+}$, and Fe$^{2+}$ were derived from the water solution made up of FeCl$_3$, NaCl, KCl, AgNO$_3$, Hg(NO$_3$)$_2$, CdCl$_2$, CoCl$_2$, CuSO$_4$, CrCl$_3$, MnCl$_2$, BaCl$_2$, ZnSO$_4$, NiCl$_2$, Mn(NO$_3$)$_2$, CaCl$_2$, PbCl$_2$, AlCl$_3$, and FeCl$_3$, respectively. These inorganic salts (AR) were purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). Ultrapure water (18.25 MΩ cm) was used throughout in this work.

4.2. Apparatus. Three-dimensional (3D) fluorescence spectra and two-dimensional (2D) fluorescence measurements were conducted by an F-7000 spectrofluorometer (Hitachi, Japan). The fluorescence experiment with a 500 nm longpass filter was conducted on FluoroMax-4 spectrofluorimeter (HORIBA, Japan). The fluorescence lifetime decay was monitored on an Edinburgh Instruments FL920 luminescence spectrometer equipped with a 280 nm laser as excitation light source. UV–vis absorption spectra were tested on a TU-1901 spectrophotometer (Beijing Purkinje General Instrument Co., Ltd.). The measurements of FT-IR spectra were on an Alpha-T spectrophotometer (Bruker, Germany). The operation of freeze drying was carried out on an FDU-1200 freeze dryer (Eyela, Japan). The measurement of pH values was conducted with a PHS-3C acidity meter (Leici, China).

4.3. Fluorescence Measurements. For the 2D fluorescence spectra, the photomultiplier (PMT) voltages were set as 700 V ($\lambda_{ex}/\lambda_{em}$ = 355–600 nm/280–400 nm) for LExL and 400 V ($\lambda_{ex}/\lambda_{em}$ = 200–308 nm/200–550 nm) for SL, respectively. The scanning speed was 12 000 nm/min. The 2D fluorescence test parameters were set as follows: excitation and emission slit widths, 10 nm; scan speed, 240 nm/min; PMT voltages, 700 V for LExL and 400 V for SL, respectively. Their DOI: 10.1021/acsomega.9b00791
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positions of emission peaks are both at 317 nm. The longpass filter of 500 nm was placed in the excitation channel to eliminate the second-order diffraction light at 282 (565/2) nm from light source. The excitation and emission slits of the FluoroMax-4 spectrophotometer are 7 nm and the integration time is 0.10 s. The quartz cuvette (1 cm × 1 cm) was used. The fluorescent signal values of DA are expressed as $I_{ex}$ and $I_{em}$ for LExL and SL, respectively.

4.4. Fluorescence Lifetime. For all the samples, the excitation wavelengths of fluorescence lifetime tests were set at 280 nm. The test results were fitted with a single exponential function, and the fitting quality is evaluated by the value of $\chi^2$.

4.5. FT-IR Spectra. The mixture solution of DA (500 μL 1.0 mmol L$^{-1}$) and Fe$^{3+}$ (1.5 mL 10 mmol L$^{-1}$) in a 5 mL beaker was freeze-dried for 72 h at $-40$ °C to obtain solid products. In addition, the KBr pressed pellet method was conducted for the FT-IR spectrum measurement.

4.6. Detection of Fe$^{3+}$. Appropriate amounts of Fe$^{3+}$ were added into 1.0 mL of DA solution (0.10 mmol L$^{-1}$). The mixture was diluted to 10 mL with water and fully mixed. Fluorescence measurements were conducted after incubation of 2 min. $I_{ex}$ and $I_{em}$ are the signal intensities of LExL and SL for the DA–Fe$^{3+}$ system, respectively. To improve the accuracy for the determination of Fe$^{3+}$, the test results were carried out in triplicate.

4.7. Real Water Sample Assays. Real water samples were taken from the Daming Lake and tap water in Ji’nan of Shandong province, China. The water of the Daming Lake was filtered via a qualitative filter in the excitation channel; Stern–Volmer curves of LExL and SL of DA–Fe$^{3+}$ system at three temperatures; fluorescence lifetime decay curves of system; FT-IR spectra of DA and DA–Fe$^{3+}$, LExL and SL emission spectra of DA, DA–EDTA, DA–EDTA–Fe$^{3+}$, PDA–EDTA–Fe$^{3+}$, PDA–Fe$^{3+}$, and DA–Fe$^{3+}$; effect of incubation time on LExL and SL of DA; quenching parameters of the DA–Fe$^{3+}$ system at three temperatures; comparison of some reported methods with our work; detection of Fe$^{3+}$ in actual water samples; theoretical calculation of TPA cross sections; lowest energy conformers of protonated DA; and TPA properties, optimized atomic coordinates, and their energies (PDF).

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.9b00791.

LExL and SL spectra of DA at different excitation wavelengths; emission spectrum of DA with a 500 nm longpass filter in the excitation channel; Stern–Volmer curves of LExL and SL of DA–Fe$^{3+}$ system at three temperatures; fluorescence lifetime decay curves of system; FT-IR spectra of DA and DA–Fe$^{3+}$; LExL and SL emission spectra of DA, DA–EDTA, DA–EDTA–Fe$^{3+}$, PDA–EDTA–Fe$^{3+}$, PDA–Fe$^{3+}$, and DA–Fe$^{3+}$; effect of incubation time on LExL and SL of DA; quenching parameters of the DA–Fe$^{3+}$ system at three temperatures; comparison of some reported methods with our work; detection of Fe$^{3+}$ in actual water samples; theoretical calculation of TPA cross sections; lowest energy conformers of protonated DA; and TPA properties, optimized atomic coordinates, and their energies (PDF).

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Notes

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