

Tunable Amphiphilicity and Multifunctional Applications of Ionic-Liquid-Modified Carbon Quantum Dots

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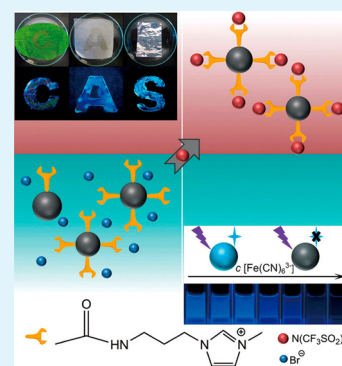
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S Supporting Information

ABSTRACT: During the past decade, increasing attention has been paid to photoluminescent nanocarbon materials, namely, carbon quantum dots (CQDs). It is gradually accepted that surface engineering plays a key role in regulating the properties and hence the applications of the CQDs. In this paper, we prepared highly charged CQDs through a one-pot pyrolysis with citric acid as carbon source and a room-temperature imidazolium-based ionic liquid as capping agent. The as-prepared CQDs exhibit high quantum yields up to 25.1% and are stable under various environments. In addition, the amphiphilicity of the CQDs can be facily tuned by anion exchange, which leads to a spontaneous phase transfer between water and oil phase. The promising applications of the CQDs as ion sensors and fluorescent inks have been demonstrated. In both cases, these ionic-liquid-modified CQDs were found to possess novel characteristics and/or superior functions compared to existing ones.

KEYWORDS: carbon quantum dots, ionic liquid, ion sensor, amphiphilicity, phase transfer, fluorescent ink



INTRODUCTION

Since accidentally found in 2004¹ and the first intended synthesis in 2006,² carbon quantum dots (CQDs) have rapidly attracted great research interest due to their unique properties and potential applications. As a rising star in the family of luminescent materials, CQDs exhibit superior biocompatibility to semiconductor quantum dots and rare elements, much higher stability of photoemission in various environments than fluorescent dyes, and a lower cost over noble metal clusters. This makes CQDs promising alternatives in a variety of applications including fluorescence imaging and sensing.^{3,4} To date, a large number of CQDs have been successfully prepared through both “top-down” and “bottom-up” methodologies, among which pyrolysis exhibits a variety of advantages due to its simplicity and high efficiency.^{5,6} As the synthetic methods gradually mature, it becomes urgent to develop efficient postfunctionalization strategies to tune and further optimize the properties of CQDs and hence to broaden their practical applications.

In this respect, noncovalent postfunctionalization through electrostatic interaction is a promising methodology. It is advantageous compared to the covalent method which is normally time-consuming. Such a strategy has been successfully applied to create nanoscale ionic materials (NIMs)⁷ containing fullerene,⁸ carbon nanotubes,^{9,10} and graphene.^{11–13} However, application of this method to CQDs is still in its infancy. For this purpose, CQDs with specially designed surfaces are

needed, since the intrinsic surface charges of the as-prepared CQDs are not sufficient for the subsequent electrostatically driven postfunctionalization. Unfortunately, the surfaces of most reported CQDs are covered by neutral polymers or small molecules, which results in a low surface charge density of the CQDs. Currently, investigations on CQDs with high surface charge densities are quite rare. Giannelis et al. prepared negatively charged CQDs by pyrolyzing citric acid at the presence of an ammonium carboxylate salt. Subsequent exchange of the small counterion with a bulky surface active cation produced organophilic (i.e., hydrophobic) CQDs which are dispersible in tetrahydrofuran.⁵ However, no applications of the organophilic CQDs have been evaluated and the quantum yield of the CQDs needs to be improved. Huang et al. also constructed carboxylate CQDs which were then utilized for selective detection of phosphate.¹⁴ Qu et al. constructed positively charged CQDs by pyrolyzing two imidazolium-based ionic liquids and examined their applications as ion sensors and cell labeling agents.¹⁵ In the last two cases, however, no counterion exchange was performed and evaluation on the potential applications of the CQDs in other respects such as fluorescent inks is absent. In another work, Wang et al. prepared carbon dots using an electrochemical method in

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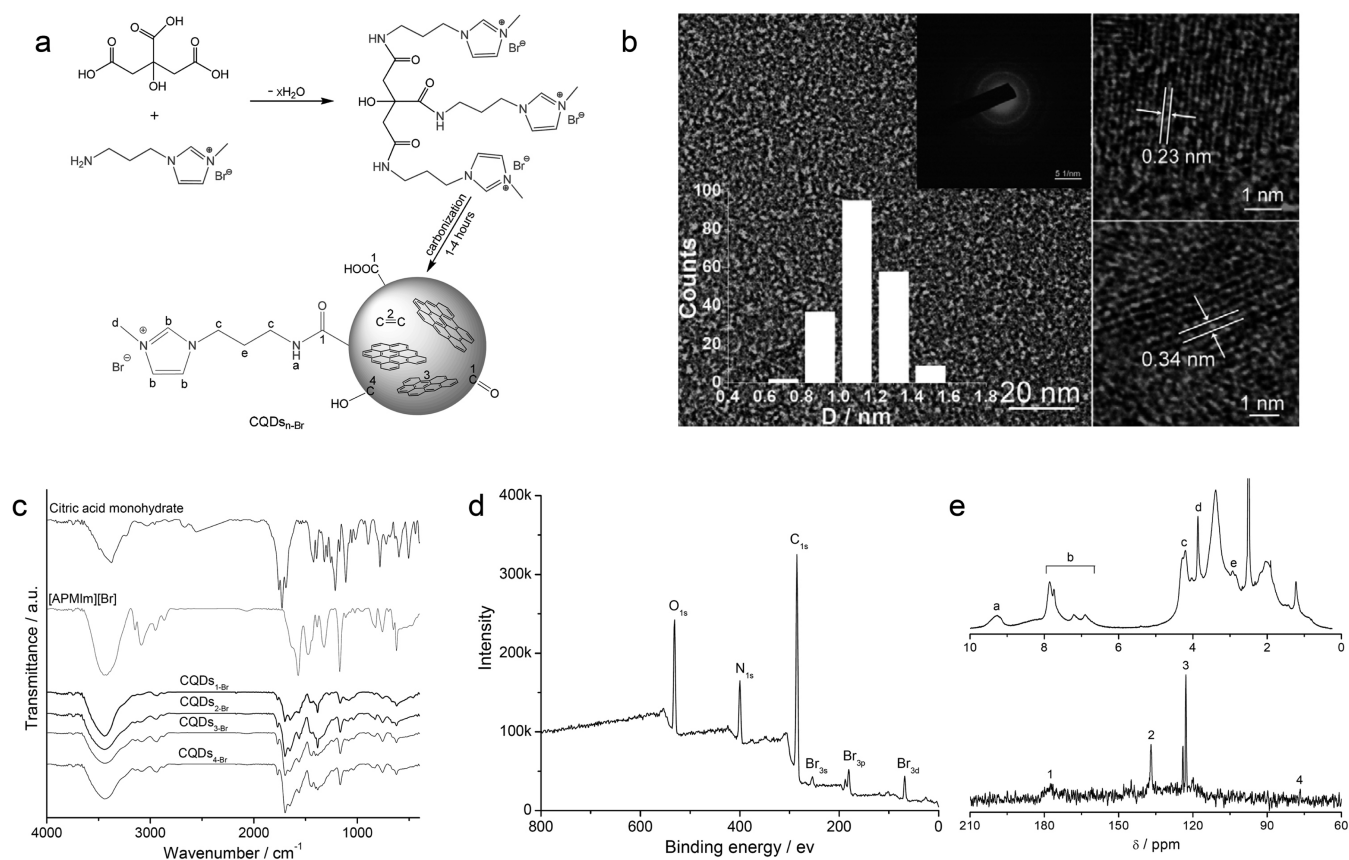


Figure 1. (a) Schematic illustration of formation procedures of $\text{CQDs}_{n-\text{Br}}$. (b) HRTEM images of $\text{CQDs}_{2-\text{Br}}$ (insets are SAED pattern and the size distribution). (c) FTIR spectra of the starting materials and $\text{CQDs}_{n-\text{Br}}$. (d, e) XPS (d), ^1H NMR (e, top), and ^{13}C NMR (e, bottom) spectra of $\text{CQDs}_{2-\text{Br}}$.

imidazolium-based ionic liquids.¹⁶ But the obtained carbon dots cannot be distinguished as CQDs, since necessary spectroscopic data were missing. Therefore, systematic work is urgently needed for charged CQDs and their postfunctionalizations to fully reveal their characteristics and potential applications.

Herein, we prepared cationic CQDs through a one-pot pyrolysis using citric acid as carbon source and a functional ionic liquid (1-aminopropyl-3-methylimidazolium bromide, [APMIm][Br]) as capping agent. The CQDs have fairly good photoluminescent (PL) properties and unique responses in ion detection. In addition, we will show that the amphiphilicity of the CQDs can be facilely tuned by anion exchange and phase transfer, and the hydrophobic CQDs could be developed into a new generation of fluorescent ink.

RESULTS AND DISCUSSION

The synthesis of [APMIm][Br]-modified CQDs follows the general procedures in pyrolysis. In brief, citric acid monohydrate and [APMIm][Br] with a molar ratio of 1:3.5 were premixed in water, which was subsequently dried and subjected to pyrolysis (for details, see Methods). No CQDs could be generated at 180–240 °C. After dialysis, the solution is colorless and remains silent under UV irradiation (Figure S1 in Supporting Information). When the temperature was raised to 260 °C, CQDs which emit strong blue light under UV irradiation were obtained (Figure S1), indicating dehydration and carbonization have occurred for the molecular precursors (Figure 1a). When the pyrolysis time was varied from 1 h to 2,

3, and 4 h, the corresponding yield of the CQDs (denoted as $\text{CQDs}_{n-\text{Br}}$ hereafter, $n = 1, 2, 3, 4$) increased from 2.03% to 10.28%, 19.72%, and 27.66%, respectively. This indicates that prolonged pyrolysis time resulted in a heavier carbonization, which was further supported by the elemental analysis where a continuous increase of carbon content and C/N ratio was noticed (Table S1). High-resolution transmission electron microscopy (HRTEM) images revealed the formation of small CQDs with the cores ranging from 0.6 to 1.6 nm (Figure 1b and Figure S2). It should be noted that the difference in sizes of $\text{CQDs}_{n-\text{Br}}$ is not so obvious considering the huge differences between the yields. Thus, it turns out that the higher yield in prolonged pyrolysis time mainly originates from the increase of the quantity of the $\text{CQDs}_{n-\text{Br}}$. The small sizes and rather narrow size distributions of $\text{CQDs}_{n-\text{Br}}$ should be ascribed to the restriction of particle growth during pyrolysis by the relatively bulky cationic imidazolium headgroups.

Most of the dots are amorphous, proved by the X-ray diffraction (XRD) measurements where only a broad peak centered at 24° (0.37 nm) has been detected (Figure S3). However, existence of crystalline structures has also been found in some cases, as evidenced from selected area electron diffraction (SAED) pattern (inset of Figure 1b) and the magnified HRTEM images (Figure 1b) of $\text{CQDs}_{2-\text{Br}}$ where well-resolved lattice fringes with interplanar spacings of 0.23 and 0.34 nm were noticed which can be assigned to (100) and (002) facets of graphite.^{3,17} Fourier transform infrared (FTIR) spectra of $\text{CQDs}_{n-\text{Br}}$ give a variety of peaks at 1768, 1700, 1650, 1562, and 1384 cm^{-1} (Figure 1c), which can be assigned to the

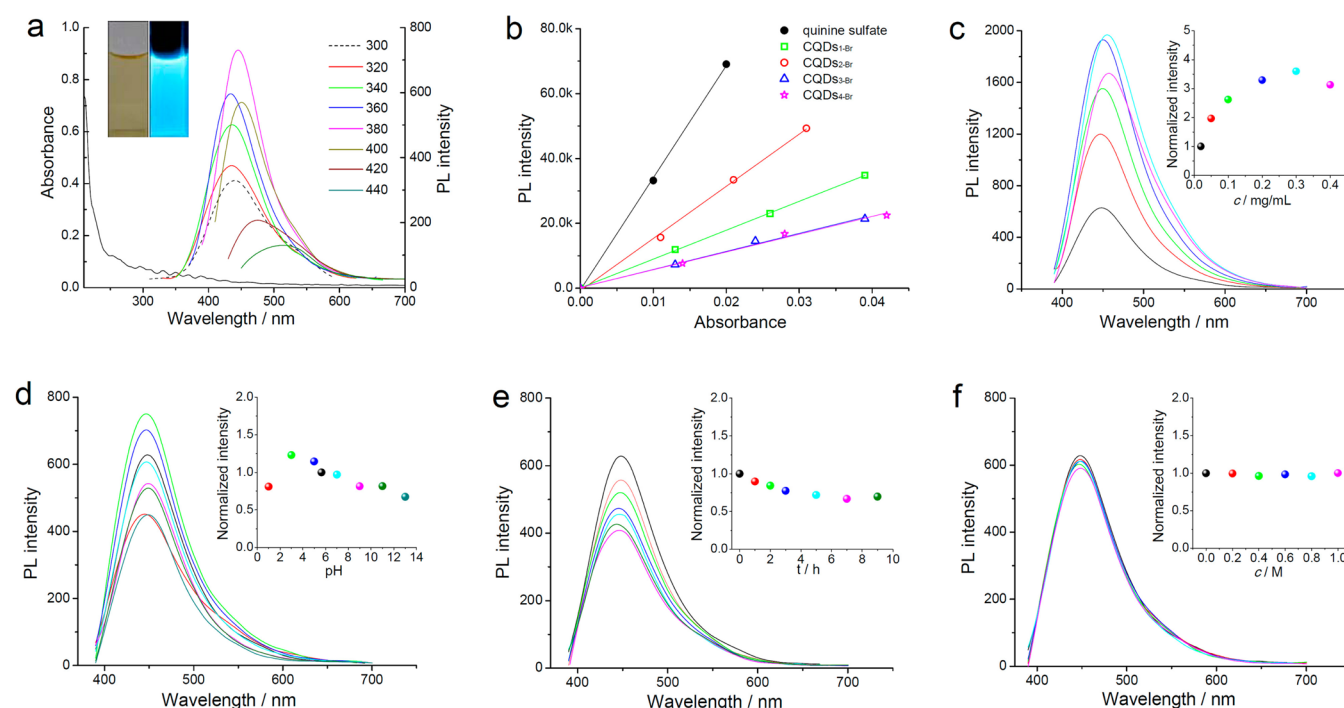


Figure 2. (a) UV-vis absorption and PL emission spectra at different excitation wavelengths of $\text{CQDs}_{2-\text{Br}}$ in water (0.02 mg/mL). Insets are photos of a typical sample under room light and UV irradiation, respectively. (b) PL intensities of aqueous solutions of quinine sulfate and $\text{CQDs}_{n-\text{Br}}$ varying with absorbance. The excitation wavelength is 360 nm for quinine sulfate and 380 nm for the $\text{CQDs}_{n-\text{Br}}$, respectively. The lines are guides for the eyes. (c–f) PL emission spectra of $\text{CQDs}_{2-\text{Br}}$ in aqueous solutions excited at 380 nm upon variation of the concentration of $\text{CQDs}_{2-\text{Br}}$ (c), pH (d), UV irradiation time at 365 nm (e), and ionic strength created by NaCl (f). Insets are the variations of the normalized PL intensity under each condition.

stretching vibrations of C=O in carboxyl, ketone, and amido, stretching vibrations of C=C, and bending vibrations of –OH, respectively. Moreover, it can be seen that in the spectra of $\text{CQDs}_{n-\text{Br}}$ nearly all the peaks from citric acid vanished while those from [APMIm][Br] (such as N–H stretching vibrations at 3148 and 3088 cm^{-1} , and C–N stretching vibration at 1169 cm^{-1}) remained, indicating that during pyrolysis citric acid decomposed completely while [APMIm][Br] survived as the surface modifiers of the $\text{CQDs}_{n-\text{Br}}$ because of its high thermal stability (Figure S4).

The chemical composition and structure of $\text{CQDs}_{n-\text{Br}}$ were further analyzed by X-ray photoelectron spectroscopy (XPS) and nuclear magnetic resonance (NMR) characterizations using $\text{CQDs}_{2-\text{Br}}$ as an example. The XPS spectrum confirms that $\text{CQDs}_{2-\text{Br}}$ is composed of carbon, nitrogen, oxygen, and bromine (Figure 1d). Fine structure spectrum of C_{1s} (Figure S5) exhibits three main peaks at 284.5, 285.6, and 287.5 eV attributed to graphitic or aliphatic, nitrous, and oxygenated carbon atoms, respectively.¹⁸ Similarly, the three peaks for N_{1s} are ascribed to three kinds of N atoms in amide group and imidazole ring. Specifically, the presence of nitrogen and bromine proves the successful attachment of [APMIm][Br] onto the surfaces of $\text{CQDs}_{2-\text{Br}}$, which is consistent with the results from FTIR. ^1H and ^{13}C NMR spectra reveal the presence of H atoms from [APMIm][Br] and the sp^2 and sp^3 hybridized C atoms (Figure 1e), providing another support to the proposed structure of $\text{CQDs}_{n-\text{Br}}$ with a carbon core and peripheral cationic groups illustrated in Figure 1a.

$\text{CQDs}_{n-\text{Br}}$ are soluble in water and ethanol while insoluble in other organic solvents (Figure S6), indicating their hydrophilic character. The PL properties of $\text{CQDs}_{n-\text{Br}}$ in water were investigated in detail (Figure 2a and Figure S7). The small

UV-vis peaks centered at 300–400 nm are typical absorptions of polycyclic aromatic hydrocarbons in the core of $\text{CQDs}_{n-\text{Br}}$,¹⁹ which agrees well with the result derived from the ^{13}C NMR spectrum (Figure 1e). Excitation-dependent PL behaviors are found in the emission spectra of $\text{CQDs}_{n-\text{Br}}$ which is common for the fluorescent carbon materials.^{20,21} In addition, all four $\text{CQDs}_{n-\text{Br}}$ exhibit the strongest PL emission at 440 nm under 380 nm excitation. Despite the similarity of the above-mentioned PL property, however, the fluorescence quantum yields (ϕ) of $\text{CQDs}_{n-\text{Br}}$ were found to be quite different. By use of quinine sulfate as reference, ϕ of $\text{CQDs}_{1-\text{Br}}$, $\text{CQDs}_{2-\text{Br}}$, $\text{CQDs}_{3-\text{Br}}$ and $\text{CQDs}_{4-\text{Br}}$ (excited at 380 nm) is calculated to be 13.9%, 25.1%, 8.7%, and 8.5%, respectively (Figure 2b). Thus, ϕ is very sensitive to the pyrolysis time, and the optimized one is 2 h at 260 °C. The detailed reason is currently unknown. In fact, though great progress has been made on CQDs during the past decade, the detailed mechanism on the origin of their PL properties is still an open question. It is generally accepted that the PL properties of the CQDs are closely related to their surface states, where any disturbance would change dramatically the PL properties of the CQDs.¹⁷

With the highest ϕ , $\text{CQDs}_{2-\text{Br}}$ was selected for further investigations. Influences of $\text{CQDs}_{2-\text{Br}}$ concentration, pH, UV irradiation at 365 nm (Hg lamp, 220 V, 50 Hz, 16 W), and ionic strength created by NaCl on the PL properties of $\text{CQDs}_{2-\text{Br}}$ were explored. With increasing $\text{CQDs}_{2-\text{Br}}$ concentration, the normalized PL intensity first increases and then decreases with a maximum around 0.3 mg/mL (Figure 2c). Meanwhile, a red shift in the emission spectra was noticed. When pH was changed from 1 to 13, the normalized PL intensity of $\text{CQDs}_{2-\text{Br}}$ varies between 0.7 and 1.2 with a maximum occurring around pH = 3.2 (Figure 2d). No

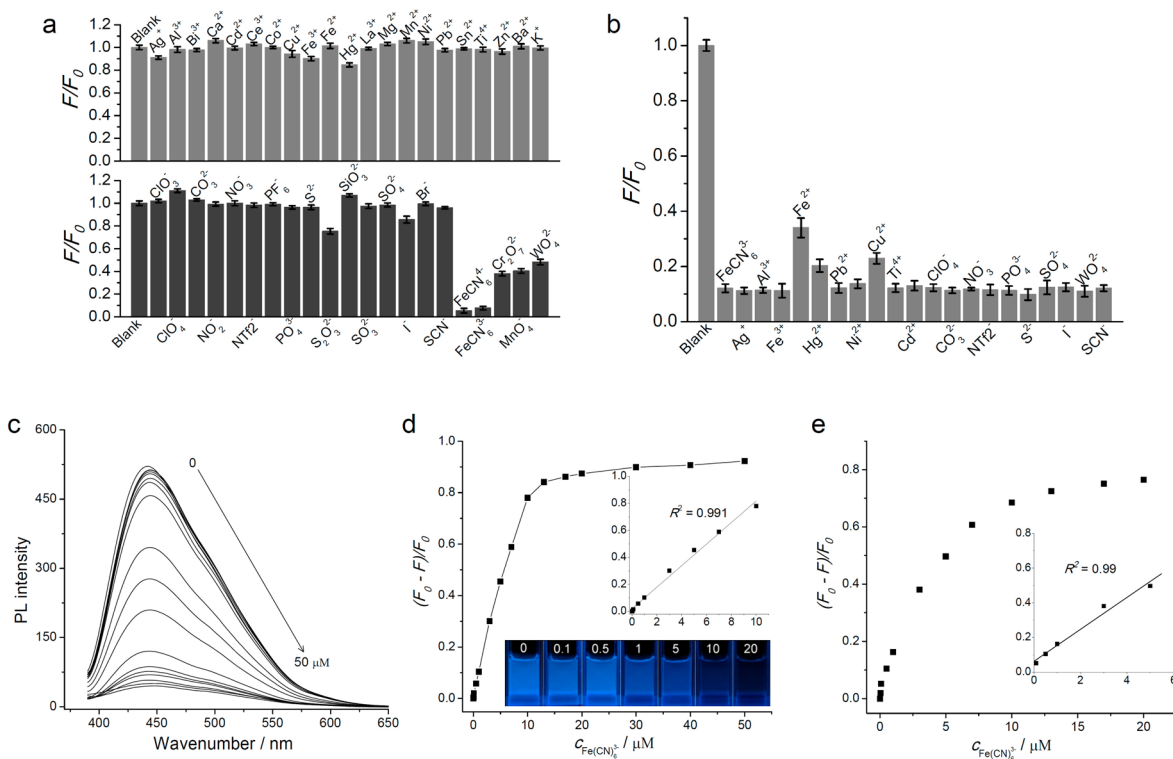


Figure 3. (a) Fluorescence response of 0.02 mg/mL CQDs_{2-Br} in 50 mM HAC–NaAc buffer solution in the presence of various ions (50 mM). (b) Competition experiments with subsequent addition of 30 mM Fe(CN)₆³⁻ to the solutions containing selected ions (50 mM). (c) Emission spectra with excitation at 380 nm and (d) fluorescence quenching degree ($(F_0 - F)/F_0$) of CQDs_{2-Br} as a function of the concentration of Fe(CN)₆³⁻ ($c_{\text{Fe(CN)}_6^{3-}}$). Insets of (d) are the magnification of the linear part of the expression of $(F_0 - F)/F_0$ against $c_{\text{Fe(CN)}_6^{3-}}$ (top) and photos of typical samples under UV light at selected $c_{\text{Fe(CN)}_6^{3-}}$ as indicated (bottom). (e) Variation of $(F_0 - F)/F_0$ as a function of the concentration of Fe(CN)₆³⁻ ($c_{\text{Fe(CN)}_6^{3-}}$) in the water from Daming Lake. Inset is the linearity of the expression $(F_0 - F)/F_0$ against $c_{\text{Fe(CN)}_6^{3-}}$.

precipitation was noticed during the whole pH range, which is advantageous to the carboxylate-group-modified CQDs which tend to precipitate at acidic conditions⁵ and the amine-modified ones where obvious fluorescence quenching was observed upon varying pH.²² After UV irradiation for 9 h, the normalized PL intensity of CQDs_{2-Br} is still higher than 0.7, reflecting their good stability of the photoemission (Figure 2e). This is valuable, since some reported CQDs with high ϕ were found to undergo undesired photobleaching.²² In addition, CQDs_{2-Br} also exhibits a high stability of the photoemission toward ionic strength. As can be seen from Figure 2f, the normalized PL intensity remains constant (close to 1) upon addition of NaCl up to 1 M. This is astonishing because according to the well-known DLVO theory, an increase in the ionic strength will lower the stability of the charged colloids by shielding the electrostatic repulsion. The [APMIm][Br]-modified CQDs possess many peripheral bulky imidazolium cations where the positive charges are delocalized, which will help to reduce the binding of small counterions. At the same time, the bulky imidazolium cations may also create a steric stabilization effect, accounting for the observed high stability.

Besides their well-known applications in bioimaging, CQDs have also been developed into novel fluorescence sensors.^{14,15,18,22–30} To reveal the potential as a novel ion sensor, the response of CQDs_{2-Br} to various cations and anions has been examined. It was found that the PL intensity of CQDs_{2-Br} only changed slightly at the presence of all the tested cations and the anions with relatively small sizes (Figure 3a). This again confirms the high stability of the photoemission of CQDs_{2-Br} in saline water. However, when the bulky metal-containing anions

are present, obvious fluorescence quenching has been observed. The most effective anions for fluorescence quenching are Fe(CN)₆³⁻ and Fe(CN)₆⁴⁻. Further examination reveals that the fluorescence quenching of CQDs_{2-Br} by Fe(CN)₆³⁻ shows considerable anti-interference against both cations and anions (Figure 3b). Therefore, a selective sensing platform toward Fe(CN)₆³⁻ and Fe(CN)₆⁴⁻ can be constructed. To get further details, the sensitivity of this sensor was evaluated and the detection limit for Fe(CN)₆³⁻ was calculated to be 10 nM based on the ratio of signal-to-noise of 3 (Figure 3c,d). Although CQDs have been successfully used to sense various metal cations,^{15,18,22–30} direct sensing of anions has not been realized. Compared to a previously reported CQDs-based sensor toward phosphate,¹⁴ our sensor can be used directly without using any third-party element. The unique properties of the [APMIm][Br]-modified CQDs in ion-sensing can be ascribed to their highly positively charged surfaces, which could only be effectively occupied by bulky anions. This assumption gets further proof when Fe(CN)₆³⁻ was changed to another well-known bulky anion, i.e., N(CF₃SO₂)₂⁻ (NTf₂, see below).

With a good selectivity, excellent anti-interference performance, and a high sensitivity, the sensor demonstrated here manifests alluring perspective in practical applications. Determination of Fe(CN)₆³⁻ in the water from Daming Lake in Jinan (China) was then carried out. The samples to be determined were filtered through a membrane (0.22 μm) and centrifuged (12 000 r/min) for 10 min prior to use. From the curve of $(F_0 - F)/F_0$ against the concentration of Fe(CN)₆³⁻ ($c_{\text{Fe(CN)}_6^{3-}}$), a well-resolved linear part ($R^2 = 0.99$) was found in the $c_{\text{Fe(CN)}_6^{3-}}$ range of 0.1–5 μM (Figure 3e) which corresponds to a

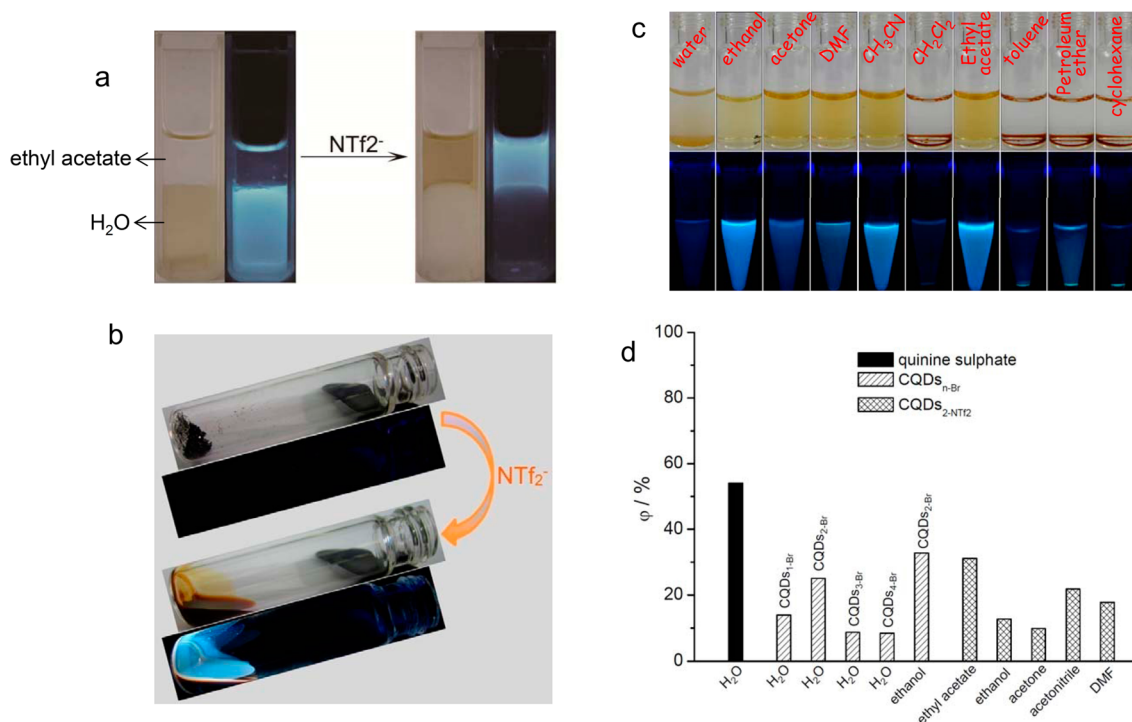


Figure 4. (a) Phase transfer from the hydrophilic CQDs_{2-Br} to the hydrophobic CQDs_{2-NTf2}. (b) Appearance of CQDs_{2-Br} and CQDs_{2-NTf2} in the solvent-free state under room light and UV irradiation. (c) Photos under room light (top) and UV irradiation (bottom) of CQDs_{2-NTf2} in various solvents. (d) ϕ of CQDs_{n-Br} and CQDs_{2-NTf2} in various solvents using quinine sulfate as reference. The excitation wavelength is 380 nm in water and 360 nm in organic solvents.

relatively high sensitivity of 41 nM. This demonstrates that our CQDs-based sensor can be used in real sample detection.

As the importance of hydrophilic CQDs is obvious, preparation of hydrophobic ones is also promising considering their potential applications in optoelectronic devices such as polymer solar cells where the active components are usually premixed in nonpolar organic solvents.^{31,32} The structural features of the [APMIm][Br]-modified CQDs open the possibility to tune their amphiphilicity by exchanging the small Br⁻ to a bulky anion, i.e., N(CF₃SO₂)₂⁻ (NTf₂⁻), which is known to form molten salts preferentially dissolving in apolar solvents.³³ When ethyl acetate was added to an aqueous solution of CQDs_{2-Br} (0.05 mg/mL), a two-phase system formed. Upon addition of excess LiNTf₂, a spontaneous phase transfer occurred for the CQDs from the bottom aqueous phase to the top ethyl acetate phase (Figure 4a), indicating that the hydrophilic CQDs_{2-Br} has been successfully transferred to the hydrophobic CQDs_{2-NTf2}. The anion exchange also alters the thermal decomposition behavior (Figure S8) and the appearance of the CQDs in solvent-free states. While CQDs_{2-Br} is a powder, CQDs_{2-NTf2} appears as a viscous fluid (Figure 4b), indicating that the anion exchange lowers the melting point of the CQDs. As expected, CQDs_{2-NTf2} loses solubility in water and is only slightly soluble in polar organic solvents such as ethanol. Instead, it can be easily redissolved in ethyl acetate and also can be well-dispersed in acetone, acetonitrile, and DMF (Figure 4c). Compared to the PL properties of CQDs_{2-Br} in water, the excitation wavelength at which the strongest emission occurs for CQDs_{2-NTf2} in various organic solvents blue shifts to 360 nm. Correspondingly, the position of the strongest emission also blue-shifts to 430 nm (Figure S9). A ϕ of 31.2% is found in ethyl acetate, which is slightly higher than that of CQDs_{2-Br} in water. In acetonitrile and DMF, similar

values of ϕ were noticed compared to that of CQDs_{2-Br} in water, while in ethanol and acetone, much lower values were found (Figure 4d). These differences should originate from the different surface and disperse states for CQDs_{2-NTf2} induced by the solvents.

The change of the state in solvent-free condition as evidenced from Figure 4b also implies that current strategy can provide an alternative way to prepare carbon-based NIMs.⁷ To the best of our knowledge, this is the first example of room temperature, solvent-free CQDs-based fluid NIMs. Fluid CQDs are expected to be advantageous compared to the powdered ones, since in most cases the fluorescence of CQDs was found to be quenched in dry state.^{19,22,34} In the current case, it is already obvious by visual inspection where the fluid CQDs_{2-NTf2} is fluorescent while the solid CQDs_{2-Br} is not (Figure 4b). To further test this assumption, CQDs_{2-NTf2} in ethyl acetate was applied as a fluorescent ink with which letters were written on various surfaces by a brush pen. It was found that the letters exhibit intense fluorescence under UV irradiation on all the tested surfaces even when they are totally dried (Figure 5). In contrast, those written by CQDs_{2-Br} in water remain silent under UV irradiation on most surfaces except paper where weak fluorescence was noticed (Figure S10). The different fluorescent performance between CQDs_{2-Br} and CQDs_{2-NTf2} should be attributed to their different aggregation tendency in solvent-free state. In the powdered CQDs_{2-Br}, the cores of the CQDs may aggregate to form clusters, leading to self-quenching of the fluorescence. However, this effect is absent in the fluid CQDs_{2-NTf2}, since the cores of the CQDs can be well separated. This result is consistent with the relatively strong fluorescence of the amine-coated fluid CQDs³⁵ and also reminiscent of the solvent-free, room temperature fluorescent molecular fluids containing π -conjugated moieties.^{36,37} Thus, as

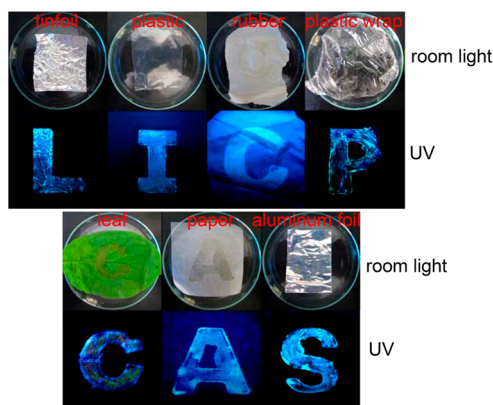


Figure 5. Photos of different letters under room light and UV irradiation directly written on various surfaces by a brush pen using $\text{CQDs}_{\text{S}_2\text{-NTf}_2}$ in ethyl acetate (0.5 mg/mL) as ink.

a new kind of fluorescent ink, $\text{CQDs}_{\text{S}_2\text{-NTf}_2}$ is expected to be writable on various surfaces and shows broad application prospects in fields of anticounterfeiting and information encryption.

CONCLUSION

In summary, we have introduced a facile strategy to prepare positively charged CQDs modified by an ionic liquid (i.e., $[\text{APMIm}][\text{Br}]$) by a one-step pyrolysis. The characteristics of the CQDs have been revealed, including a small and narrow size distribution, a high ϕ , high stability of photoemission under UV irradiation and in saline water. In addition, the CQDs can be postfunctionalized and their amphiphilicity can be tuned by a noncovalent method, i.e., counterion exchange, which is superior to the covalent method that is usually time-consuming. With all of these merits, the $[\text{APMIm}][\text{Br}]$ -modified CQDs exhibit a variety of potential applications. Specifically, a fluorescence sensor toward $\text{Fe}(\text{CN})_6^{3-}$ and $\text{Fe}(\text{CN})_6^{4-}$ can be constructed using $\text{CQDs}_{\text{S}_2\text{-Br}}$ because of its good selectivity and low detection limit. For another example, the fluid $\text{CQDs}_{\text{S}_2\text{-NTf}_2}$ shows promise as a fluorescent ink which can be written on various surfaces based on its strong fluorescence in solvent-free state. Considering the wide range of precursors can be selected for CQDs synthesis and that of anions can be adopted in counterion exchange, the properties of the ionic-liquid-modified CQDs could be further optimized and their applications in different fields are yet to be broadened. We believe that the concept proposed here will trigger intense interests and open a new avenue in the research of CQDs.

METHODS

Synthesis of $\text{CQDs}_{\text{n-Br}}$. To a round-bottom flask containing 20 mL of water, citric acid monohydrate (1.0 g) and $[\text{APMIm}][\text{Br}]$ (3.67 g) with a molar ratio of 1:3.5 were added. After citric acid monohydrate and $[\text{APMIm}][\text{Br}]$ dissolved totally, water was removed by rotary evaporation and a faint yellow gel was obtained, which was then immersed in an oil bath and pyrolyzed at 180–260 °C for 1–4 h under argon and magnetic stirring. After cooling to room temperature, 25 mL of water was added and a reddish brown dispersion was gained, which was then dialyzed by a dialysis bag (1000 Da) against water for 3 days to remove the molecular precursors. Finally, the water of the dialyzate was eliminated by rotary evaporation and the ionic-liquid-modified $\text{CQDs}_{\text{n-Br}}$ was obtained as a brown powder.

Quantum Yield Measurements. Quantum yield (ϕ) determination was achieved according to previously established procedure by comparing their integrated PL intensities. Quinine sulfate in 0.1 M

H_2SO_4 (quantum yield, 54%) was chosen as a standard. The absorbance of the solutions of CQDs and reference sample was kept below 0.10 at 380 and 360 nm. The quantum yields of the CQDs were achieved by the following equation:

$$\phi_c = \phi_q (F_c/A_c)(A_q/F_q)(\eta_c/\eta_q)^2$$

where the subscripts “c” and “q” refer to CQDs and quinine sulfate, respectively. ϕ is the PL quantum yield. A is the absorbance at the excitation wavelength. F is the integrated PL intensities, and η is the refractive index of the solvent.

Fluorescence Sensor. A solution of $\text{CQDs}_{\text{S}_2\text{-Br}}$ (0.02 mg/mL) in 50 mM HAc-NaAc buffer solution (pH = 3.2) was prepared and used as a fluorescence sensor toward $\text{Fe}(\text{CN})_6^{3-}$ and $\text{Fe}(\text{CN})_6^{4-}$. For the detection of $\text{Fe}(\text{CN})_6^{3-}$ in real samples, the water obtained from Daming Lake (Jinan, China) was used after filtering through a membrane (0.22 μm) and centrifuging at 12 000 r/min for 10 min. The changes of the PL intensities of the CQDs were evaluated by F/F_0 or $(F_0 - F)/F_0$, where F_0 and F are PL intensities before and after addition of the target ion, respectively.

Phase Transfer. For the preparation of hydrophobic $\text{CQDs}_{\text{S}_2\text{-NTf}_2}$, 30 mg of $\text{CQDs}_{\text{S}_2\text{-Br}}$ was dissolved in 15 mL of water to form a transparent solution. Then 10 mL of ethyl acetate was added to form a two-phase system with the $\text{CQDs}_{\text{S}_2\text{-Br}}$ aqueous solution at the bottom. To this system, LiNTf₂ was added gradually with constant shaking until most of the $\text{CQDs}_{\text{S}_2\text{-Br}}$ was transferred into the ethyl acetate phase. After equilibrium for half an hour, the upper ethyl acetate phase was transferred to a round-bottom flask by a separating funnel. Finally, $\text{CQDs}_{\text{S}_2\text{-NTf}_2}$ was obtained as a viscous fluid after ethyl acetate was eliminated by rotary evaporation.

Fluorescent Inks. For water-based ink, a transparent aqueous solution containing 5 mg of $\text{CQDs}_{\text{S}_2\text{-Br}}$ and 10 mL of water was prepared. Similarly, an ethyl acetate solution containing 5 mg of $\text{CQDs}_{\text{S}_2\text{-NTf}_2}$ and 10 mL of ethyl acetate was prepared as oil-based ink.

ASSOCIATED CONTENT

Supporting Information

Photos of CQDs samples and letters written by the CQDs, HRTEM images of $\text{CQDs}_{\text{S}_1\text{-Br}}$ and $\text{CQDs}_{\text{S}_3\text{-Br}}$, XRD pattern and XPS fine structure spectra of $\text{CQDs}_{\text{S}_2\text{-Br}}$, TGA of $[\text{APMIm}][\text{Br}]$, $\text{CQDs}_{\text{S}_2\text{-Br}}$ and $\text{CQDs}_{\text{S}_2\text{-NTf}_2}$, UV-vis absorption and PL emission spectra of both the hydrophilic and hydrophobic CQDs in various solvents. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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