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# The Regulation of Hydrophilicity and Hydrophobicity of Carbon Dots via One-pot Approach

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The regulation of hydrophilicity/hydrophobicity of carbon dots (CDs) at will is most important. One pot simultaneous preparation of hydrophilic and/or hydrophobic CDs is herein reported, via hydrothermal process with 1-butyl-3-methylimidazolium hexafluorophosphate as carbon source in a $H_3PO_4$-ethanol medium. The hydrophilicity or hydrophobicity of CDs (or their proportions) is simply regulated by varying the $H_3PO_4$/ethanol molar ratio. Hydrophilic and hydrophobic CDs are achieved simultaneously with $H_3PO_4$/ethanol molar ratios within 0-1.72, while hydrophilic or hydrophobic CDs are the solely product from $H_3PO_4$-$BmimPF_6$ or $BmimPF_6$-only systems. The CDs exhibit excitation-dependent maximum fluorescence at 360/440 nm (hydrophilic) and 430/510 nm (hydrophobic), with quantum yields of 17.0% and 7.7%, respectively. Both hydrophilic and hydrophobic CDs achieved by this approach exhibit favorable biocompatibility and offer great potentials in bio-imaging as demonstrated for the fluorescent labeling and imaging of live HeLa cells.

## 1. Introduction

As a kind of newly emerged fluorescent materials, fluorescent carbon nanoparticles (carbon dots, CDs) have shown promising potentials in a wide range of application fields, including sensing, bio-imaging, drug delivery, photocatalysis and electrocatalysis.[1,2] CDs exhibit tunable fluorescent emission property and chemical stability, in addition to favorable biocompatibility as well as low toxicity, they have shown promises as a new generation of fluorescence probe in the field of bio-imaging or bio-labeling.[3-9]

CDs are generally prepared via either top-down or bottom-up approaches. Top-down includes breaking down of carbon materials such as candle soot,[10] carbon nanotubes[11] or activated carbon,[12] while bottom-up includes thermal treatment of carbon-containing molecules such as glucosamine,[13] ascorbic acid,[14] citrate salt [15] and glycine,[16] polymers like PEI,[17] and biological materials like grass,[18] milk[19] and honey[20]. In most cases, hydrophilic CDs with oxygen- or nitrogen-containing groups, e.g., carboxyl, hydroxyl and amine, are obtained and directly applied to bio-imaging or chemical sensing.[12,16-20] Recently, surface engineering of CDs provides a facile approach for controlling the luminescent property of CDs and expanding its application.[21-23] Nitrogen doping is an effective approach to enhance the quantum yield of CDs, which is beneficial for the improvement of sensing sensitivity.[24-26] It has been demonstrated that higher degree of surface oxidation of CDs causes red-shift of the luminescent emission peak, making the CDs more suitable for bio-imaging and cancer therapy.[27-29] In the contrast, however, hydrophobic CDs share little attention at the present, due to both the difficulty in their fabrication [30] and the up-to-date limitations in their practical applications attributed to the incompatibility with aqueous environment. It should be noted that the compatibility of hydrophobic CDs with liposoluble cell membrane facilitates their transfer into cell interior, [31] and thus might provide better results for bio-imaging. At the present, hydrophobic CDs are usually prepared in organic solvents, e.g., octadecene and toluene, with long-chain organic molecules as surface passivation/capping agents including dodecanethiol,[31] hexadecylamine,[32] octadecylamine,[33] and organosilane.[34] Practically, hydrophobic CDs can be converted into hydrophilic ones to meet the requirement of applications in biological circumstances.[34,35]

Ionic liquids (ILs) are organic salts consisting entirely of ionic species (anions and cations) and they are recognized as ‘‘designer solvents’’ for the regulation of their physicochemical properties by flexible selection of suitable ionic components to fulfill specific demands.[36] Ionic liquid with nitrogen-containing butyl cation has been adopted as carbon source for the preparation of highly photoluminescent CDs, and the versatility of ionic liquid moieties endow the obtained CDs attracting properties.[37] CDs generated with 1-butyl-3-methylimidazolium bromide (BmimBr) and 1-butyl-3-methylimidazolium tetrafluoroborate ($BmimBF_4$) as carbon sources show different selectivity in the sensing of metal cations attributed probably to the binding affinity of metal cations with the imidazolium and hydroxyl groups on CDs surface.[37]

For practical purposes, the regulation of the hydrophilicity or hydrophobicity of CDs at will is most important and highly interesting. However, a literature survey indicated that this field remains hitherto not well exploited. In the previous studies, only one kind of carbon dots, i.e., either hydrophilic or hydrophobic carbon dots, could be obtained at one time.[21-33] The regulation of hydrophilicity/hydrophobicity of carbon dots is realized through pose-modification of the as-prepared carbon dots with target

molecules or groups.[34,35] In the present work, we report a facile approach for the regulation of producing either hydrophilic or hydrophobic CDs, or the production of both, with hydrophobic imidazolium IL 1-butyl-3-methylimidazolium hexafluorophosphate ($BmimPF_6$) as the sole carbon source in a $H_3PO_4$-ethanol medium. A simple control of the $H_3PO_4$/ethanol ratio facilitates the regulation of the hydrophilicity and/or hydrophobicity of the produced CDs (or their proportions).

## 2. Materials and Methods

### 2.1. Materials

Ionic liquids used in the present study, e.g., 1-butyl-3-methylimidazolium hexafluorophosphate ($BmimPF_6$), 1-butyl-3-methylimidazolium chloride (BmimCl), and 1-butyl-3-methylimidazolium bis((trifluoromethyl)sulfonyl)imide ($BmimNTF_2$), are purchased from Cheng Jie Chemical Co. Ltd. (Shanghai, China). Ethanol, NaOH, $H_3PO_4$, $H_2SO_4$ are obtained from Sinopharm Chemical Reagent (Shanghai, China). Quinine sulfate is the product of Aladdin Reagents Co. (Shanghai, China) and fluorescein is received from Shenyang Xinxing Chemical Reagents (Shenyang, China). Fetal bovine serum, Dulbecco's modified Eagle's medium (DMEM), penicillin, streptomycin, 3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyltetrazolium bromide (MTT) assay kit are achieved from Nanjing KeyGEN Biotech Co. Ltd. (Nanjing, China). All the reagents used are at least of analytical reagent grade unless otherwise specified. Deionized water (DI water) of 18 MΩ $cm^{-1}$ is used throughout.

### 2.2. Characterizations

UV-vis absorption spectra of the obtained CDs are recorded on a U-3900 UV-vis spectrophotometer (Hitachi High Technologies, Japan). F-7000 fluorescence spectrophotometer (Hitachi High Technologies, Japan) and Fluormax 4 fluorescence spectrophotometer (Horiba Scientific, France) are employed to record photo-luminescence behaviors. FT-IR spectra are obtained by a Nicolet-6700 spectrophotometer (Thermo Instruments Inc., USA). Transmission electron microscopy (TEM) images are recorded on a JEM-2100 high resolution transmission electron microscopy (JEOL, Japan). XPS analysis is performed on an ESCALAB 250 surface analysis system (Thermo Electron, England). X-ray diffraction (XRD) patterns are recorded on a MPDDY2094 X-ray diffractometer (PAnalytical B.V, Netherlands) with Cu-K$\alpha$ irradiation ($\lambda$=1.5406Å) in the range of 2θ from 10 to 80°. HeLa cells are cultured in HERA Cell 150 incubator (Thermo Instruments Inc., USA), and their images are obtained on an inverted fluorescent microscope (Nikon, Japan). MTT assay is conducted by using a Synergy H1 ELISA plate reader at 550 nm (BioTek, USA).

### 2.3. Preparation of hydrophilic and hydrophobic CDs

In a typical procedure, 5 mL of ionic liquid $BmimPF_6$ is mixed with 5 mL of phosphoric acid (5 mol $L^{-1}$) dissolved in pure ethanol. The mixture is then sealed into a 15-mL Teflon autoclave and heated at 200 °C for 96 h. After cooling down to room temperature, the reaction mixture is neutralized by using 0.6 mol $L^{-1}$ NaOH dissolved in ethanol. After centrifugation at 10000 rpm for 10 min, the supernatant is collected followed by concentration with rotary evaporation and dialysis against water using cellulose ester membrane (MWCO: 500-1000). The hydrophobic CDs gradually aggregate and precipitate from the water medium. After 30 min, hydrophilic CDs are moved into another cellulose ester membrane, and both hydrophobic and hydrophilic CDs are subject to further dialysis for 48 h. The final products, hydrophilic and/or hydrophobic CDs, are collected and dispersed in water and ethanol, respectively.

Different portions of hydrophilic or hydrophobic CDs are obtained by varying the molar ratio of phosphoric acid to ethanol in the range of 0-1.72, corresponding to concentration of phosphoric acid varied from 0-10 mol $L^{-1}$.

### 2.4. MTT test and cell imaging

The hydrophilic and hydrophobic CDs are dispersed in water and ethanol at the concentration of 40 mg $mL^{-1}$ and 15.3 mg $mL^{-1}$, respectively. When used for MTT assay and imaging, they are diluted into different concentrations with culture medium.

HeLa cells are cultured with a DMEM medium supplemented with 10% fetal bovine serum and 1% (v/v) penicillin/streptomycin at 37°C in a humidified environment of 5% $CO_2$.

The cytotoxicity of either hydrophilic or hydrophobic CDs achieved in the present system is investigated by using a standard MTT assay. Typically, 100 μL of suspension of HeLa cells is added to each well of a 96-well plate. The cells are first cultured for 12 h in an incubator (37 °C, 5% $CO_2$), followed by incubating for another 20 h by replacing the culture medium with 100 μL of DMEM containing various concentrations of the CDs. Afterwards, 20 μL of MTT solution (5 mg $mL^{-1}$) is added into each cell well, and the cells are further incubated for 4 h. The culture medium in the well is removed and 150 μL of DMSO is added. The mixture is shaken for 5 min at room temperature, and the absorbance (A) of the mixture is measured at 550 nm. The cell viability is estimated according to the following equation:

$$\text{Cell viability (\%)} = A_{treat}/A_{control} \times 100$$

The potential applications of the hydrophilic and hydrophobic CDs are demonstrated by the labeling of HeLa cells. HeLa cells are first cultured at 37 °C for 12 h, followed by further incubation for an extra 4 h in the presence of 2 mg $mL^{-1}$ of hydrophilic CDs or 0.05 mg $mL^{-1}$ of hydrophobic CDs. Afterwards, the medium is removed and the cells are washed thoroughly for three times with phosphate buffer (PBS, 10 mmol $L^{-1}$, pH 7.4). The HeLa cells are finally photographed with inverted fluorescence microscope at different excitation wavelengths.

## 3. Results and Discussion

### 3.1. Preparation and characterization of hydrophilic and hydrophobic CDs

HRTEM images illustrated in Figure 1 indicate uniform and monodispersed morphology for both the hydrophilic and hydrophobic CDs prepared in the $H_3PO_4$-ethanol medium, with average sizes of ca.3.8±0.7 nm and ca.6.1±0.9 nm, respectively. No lattice structure is provided for both hydrophilic and hydrophobic CDs. This is consistent with the XRD patterns illustrated in Figure S1 which show broad peaks at around 22° (2θ) corresponding to amorphous nature of the CDs.[32,35]

FT-IR spectra for the original ionic liquid ($BmimPF_6$) and

the simultaneously prepared hydrophilic and hydrophobic CDs

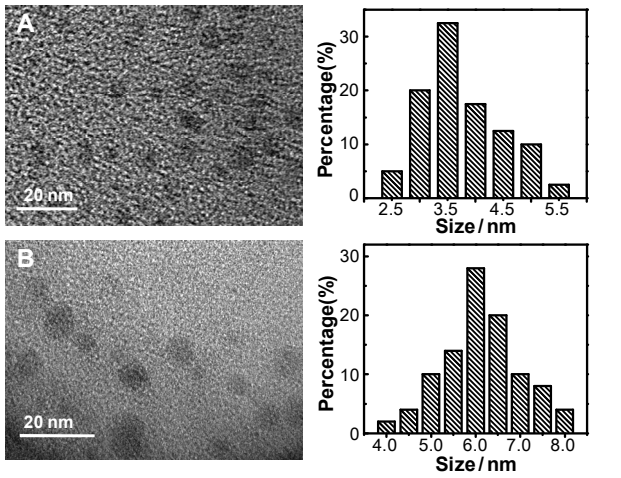



Figure 1. HRTEM images and size distribution histograms for the simultaneously prepared hydrophilic CDs (A) and hydrophobic CDs (B).

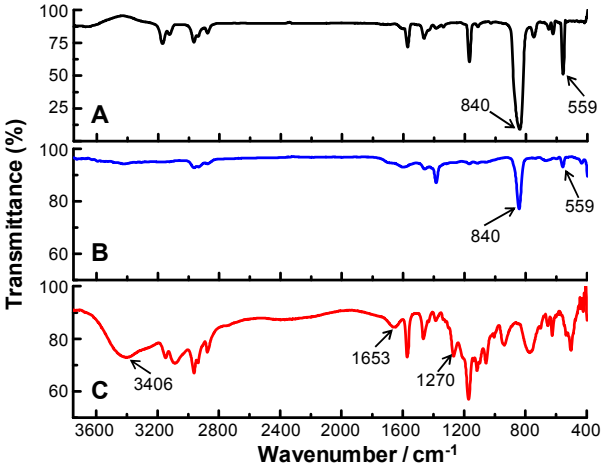



Figure 2. FT-IR spectra of the ionic liquid serving as carbon source and the simultaneously prepared CDs. (A) $BmimPF_6$, (B) hydrophobic CDs, (C) hydrophilic CDs.

are illustrated in Figure 2. It is seen that the absorption bands for the hydrophobic anionic ionic liquid moiety $PF_6^-$ at 840cm$^{-1}$ (stretching vibration) and 559cm$^{-1}$ (bending vibration) are clearly identified in the spectra for both $BmimPF_6$ and the hydrophobic CDs. On the other hand, the FT-IR spectrum of the hydrophilic CDs is characterized by the hydrophilic oxygen-containing groups, i.e., the stretching vibration absorption bands assigned to C-OH and C=O at 3406cm$^{-1}$ and 1653cm$^{-1}$ respectively, in addition to that assigned to -OH at 1270cm$^{-1}$.[13, 14] The analytical results of X-ray photoelectron spectroscopy (XPS) (Figure 3) further confirmed the presence of these functional groups in the hydrophilic and hydrophobic CDs. The P2p peak at 136.2eV and F1s peak at 686.4eV are well documented and ascribed to the $PF_6^-$ group.[38,39] These peaks are clearly observed in the hydrophobic CDs. On the other hand, the XPS spectra for the hydrophilic CDs illustrate C1s peaks at 285.9eV and 288.4eV, and O1s peaks at 531.7eV and 533.0eV (Figure S3). This observation well indicated the presence of hydroxyl and carboxyl groups.[18,40] In addition, elemental analyses are conducted for the simultaneously prepared CDs. For the hydrophilic CDs, the elemental contents are derived to be 77.61% for C, 22.03% for O, 0.3% for F and 0.06% for P, while for the hydrophobic CDs, the contents are 85.58% for C, 5.91% for O, 2.46% for F and 1.17% for P.

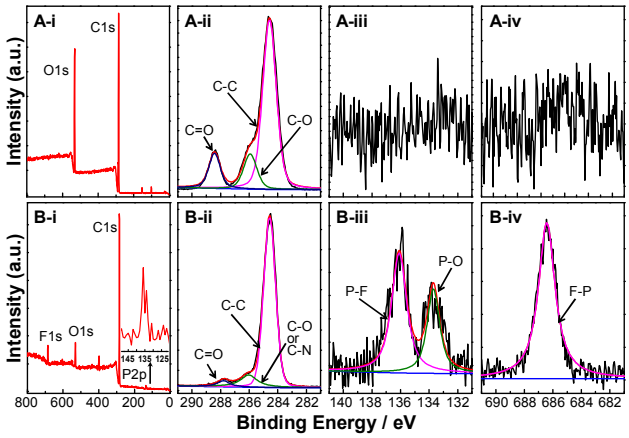



Figure 3. XPS spectra for the simultaneously prepared CDs. (A) hydrophilic CDs, (B) hydrophobic CDs. (i) raw data, (ii) high resolution spectra of C1s, (iii) P2p, (iv) F1s.

### 3.2. Photoluminescence properties of the hydrophilic and hydrophobic CDs

Figure 4 shows the UV-vis absorption and photoluminescence spectra for the prepared hydrophilic and hydrophobic CDs. In UV-vis absorption spectra of both hydrophilic and hydrophobic CDs (Figure 4A-i, 4B-i), the absorption bands with a maximum wavelength at ca. 220nm and those at around 260-270nm are attributed to the π-π* transition of the aromatic sp$^2$ domains. For the case of hydrophilic CDs, the absorptions at around 280-290 nm and 330 nm (Figure 4A) are related to the n-π* transition of C=O bond.[40,41] Figure 4A-ii and 4B-ii indicated that both hydrophilic and hydrophobic CDs clearly exhibit excitation-dependent photoluminescent emission, with maximum excitation/emission wavelengths at 360/440 nm for hydrophilic CDs and 430/510 nm for hydrophobic CDs, respectively.

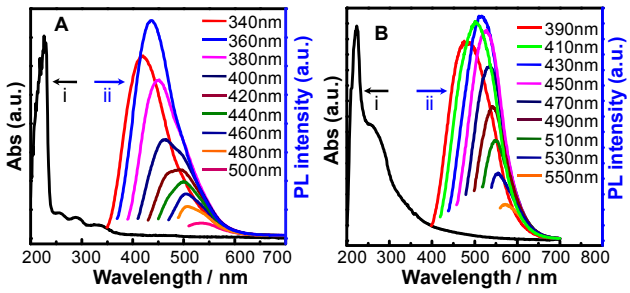


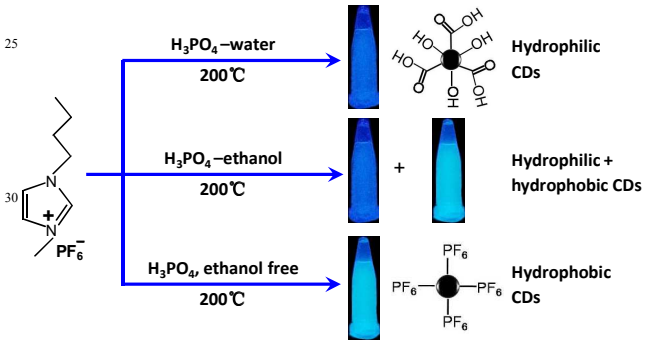

Figure 4. UV-vis absorption spectra (i) and photoluminescence spectra (ii) for the simultaneously prepared CDs. (A) hydrophilic CDs and (B) hydrophobic CDs.

The maximum wavelengths of both excitation and fluorescence for the hydrophobic CDs exhibit a 70-nm red-shift in comparison with those for the hydrophilic CDs. It has been reported that CDs with a larger size would emit at a longer wavelength,[35,42] and the

surface chemical state has been demonstrated to be an crucial factor in tuning the photoluminescent behaviors of the CDs.[27-29,43] In the present case, hydrophobic CDs not only have a larger average size of 6.1 nm with respect to 3.8 nm for the hydrophilic CDs, they also possess non-polar surface groups, which correspond to a longer excitation/emission wavelength. In addition, the quantum yields are derived to be 17.0% for the hydrophilic CDs and 7.7% for the hydrophobic CDs as given in Table S1 and Table S2.

### 3.3. Elucidations for simultaneous formation of hydrophilic and hydrophobic CDs with ionic liquid as carbon source

In the preparation of CDs, strong acids, e.g., $H_3PO_4$, $H_2SO_4$ and $HNO_3$, are generally used as oxidizing agents or catalytic agents,[7,17] and the concentration level of the corresponding acid has been demonstrated to be a decisive factor on governing the photoluminescence property of the obtained CDs.[35,44] In the present study, $H_3PO_4$ is used as catalyst and oxidizing agent at high temperature, and ethanol is adopted as the solvent for dissolving the hydrophobic ionic liquid serving as carbon source, in this particular case, $BmimPF_6$ is employed for this purpose. The reaction temperature is fixed at 200 °C in a Teflon autoclave by varying the $H_3PO_4$/ethanol molar ratio within a certain range, and very interesting results are observed.




Scheme 1. The mechanisms for regulating the formation of hydrophilic and/or hydrophobic CDs by thermal treatment of hydrophobic IL $BmimPF_6$ in a $H_3PO_4$-ethanol medium.

Our experiments further indicated that the variation of $H_3PO_4$/ethanol molar ratio within 0-1.72 gives rise to different proportions of hydrophilic and hydrophobic CDs, as illustrated in Table S3. It is also schematically illustrated in Scheme 1 that hydrophilic and hydrophobic CDs are achieved simultaneously in the $H_3PO_4$-ethanol system in the presence of $H_3PO_4$ and ethanol (with $H_3PO_4$/ethanol molar ratios of 0-1.72). However, hydrophilic CDs are the solely product harvested when there is existing only $H_3PO_4$ in the reaction system with $BmimPF_6$ as carbon source (different amounts of CDs are obtained by changing the content of $H_3PO_4$, as illustrated by 5 and 14.6 mol $L^{-1}$ in Table S3). While pure hydrophobic CDs are obtained when there is only $BmimPF_6$ in the reaction system. These observations suggest that acidic reaction environment or the presence of protons ($H^+$) might be a decisive parameter for the formation of the CDs and controlling their hydrophilicity or hydrophobicity. In a system free of $H_3PO_4$ or ethanol, the decomposition of the cationic ionic liquid moiety $Bmim^+$ under high temperature provides carbon source and facilitates the formation of CDs.

Meanwhile, the hydrophobic anionic $PF_6^-$ attaches on the formed CDs and offers them hydrophobicity. When $H_3PO_4$ is introduced into the ethanol medium, it is partially dissociated and free protons ($H^+$) are released, which leads to partial decomposition of hydrophobic $PF_6^-$ into volatile HF and $PF_5$, and in the meantime it causes the formation of carboxyl groups on the surface of CDs.[12,45,46] As a result, both hydrophilic and hydrophobic CDs are achieved in such a case, and their percentage is regulated by varying the $H_3PO_4$/ethanol molar ratio. In a pure aqueous medium, the complete dissociation of $H_3PO_4$ provides sufficient amount of protons, which facilitates thorough decomposition of $PF_6^-$ into volatile HF and $PF_5$.[46] In such a case, hydrophilic CDs are the only product.

For the purpose of demonstrating the above mechanisms, a hydrophilic ionic liquid 1-butyl-3-methylimidazolium chlorine (BmimCl) and another hydrophobic ionic liquid 1-butyl-3-methylimidazolium bis((trifluoromethyl)sulfonyl)imide ($BmimNTF_2$) are adopted respectively as carbon source for the preparation of CDs through the aforementioned hydrothermal system in a $H_3PO_4$-ethanol medium. The experiments have shown that similar results are achieved with hydrophobic $BmimNTF_2$ as the carbon source. On the other hand, however, only hydrophilic CDs are obtained when hydrophilic BmimCl is used. The photoluminescence spectra for these CDs are illustrated in Figure S4, showing similar trends as those for the CDs prepared by $BmimPF_6$. For the above three ionic liquids, they all contain imidazolium type cationic moieties, and the hydrophilicity or hydrophobicity of the CDs prepared with them as carbon sources are closely related to the features of their counter anions. That is to say the anionic moiety of the ionic liquid is among the key factors for governing the hydrophilicity or hydrophobicity of the CDs produced.

### 3.4. MTT test and cell imaging

MTT assay is used to evaluate the cytotoxicity or biocompatibility of the CDs prepared in a $H_3PO_4$-ethanol medium with thermal treatment of hydrophobic ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate ($BmimPF_6$), and the results are illustrated in Figure 5. It is clearly seen that there is no obvious variation on the cell viability at low concentration levels of both hydrophilic and hydrophobic CDs. The cell viability of ca.85% and ca.90% is maintained at 6.0 mg $mL^{-1}$ of hydrophilic CDs and 0.2 mg $mL^{-1}$ of hydrophobic CDs.

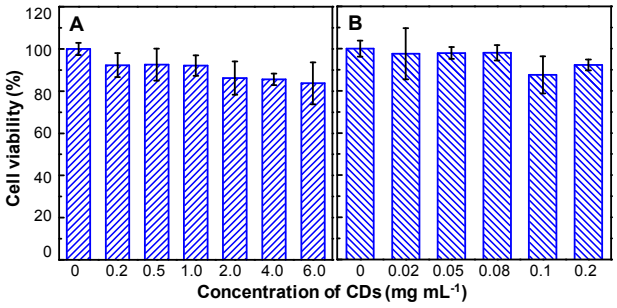



Figure 5. Viability of HeLa cells after incubation with the hydrophilic CDs (A) and hydrophobic CDs (B) prepared in a $H_3PO_4$-ethanol medium with thermal treatment of hydrophobic ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate ($BmimPF_6$).

The effect of culture medium on the PL properties of the hydrophobic CDs is also investigated. The hydrophobic CDs disperse well in the cell culture medium without causing any turbidity at a concentration of <0.75 mg $mL^{-1}$, and virtually no change on their PL properties is recorded with respect to that observed in ethanol solution (Figure S5).

The potential applications of the prepared fluorescent CDs are demonstrated by the labeling of HeLa cells. After incubating for 4 h with 2 mg $mL^{-1}$ of hydrophilic CDs and 0.05 mg $mL^{-1}$ of hydrophobic CDs, the HeLa cells are photographed with an inverted fluorescence microscope (Figure 6). Clear images are observed under excitation at 340 nm and 495 nm for both hydrophilic and hydrophobic CDs. It should be noted that when exciting at longer wavelengths of 550 nm and 595 nm, the images are hardly seen for the cells incubated with hydrophilic CDs. In the contrast, however, the images are still clearly seen under identical excitation wavelengths for the cells incubated with hydrophobic CDs. This observation is obviously attributed to the fact that hydrophobic CDs are prone to penetrate the cell membrane based on Overton' rules.[47] When applying in biological systems, fluorescent emission at a longer wavelength is preferential for the purpose of eliminating the background of living tissues and reducing the radiation damage from short-wavelength excitation on the living tissues. In general, the present study illustrates that the hydrophobic CDs exhibit favorable potentials in the field of bio-imaging/bio-labeling.

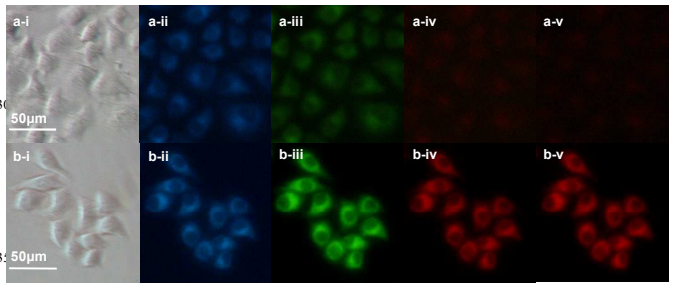



Figure 6. The photographs of HeLa cells after incubation for 4 h with 2 mg $mL^{-1}$ of hydrophilic CDs (a) and 0.05 mg $mL^{-1}$ of hydrophobic CDs (b). Taken at bright field (i); with excitation at 340 nm (ii), 495 nm (iii), 550 nm (iv) and 595 nm (v).

## 4. Conclusions

Hydrothermal treatment of hydrophobic ionic liquid in a $H_3PO_4$-ethanol medium facilitates simultaneous preparation of hydrophilic and/or hydrophobic fluorescent carbon dots. The nature of anionic moiety of the ionic liquid plays an important role in the regulation of hydrophilicity or hydrophobicity of the prepared CDs (or their proportions), which can be further regulated by varying the $H_3PO_4$/ethanol ratio in the reaction system. This study provides a new approach for the development of carbon-based materials for biological applications.

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## Notes and references

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† Electronic Supplementary Information (ESI) available: XRD patterns of the hydrophilic and hydrophobic CDs; TEM images of the hydrophilic and hydrophobic CDs at lower magnification; XPS spectrum of O1S in hydrophilic CDs; Quantum yields of CDs; Proportions of hydrophilic and hydrophobic CDs achieved by regulating the $H_3PO_4$/ethanol molar ratio; Fluorescent properties of the hydrophilic and hydrophobic CDs prepared by using hydrophilic ionic liquid BmimCl and hydrophobic ionic liquid $BmimNTF_2$ as carbon sources; Fluorescent spectra of hydrophobic CDs dispersed in ethanol and culture medium. See DOI: 10.1039/b000000x/

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## Graphical Abstract

The hydrophilicity or hydrophobicity of carbon dots is regulated by varying the $H_3PO_4$/ethanol molar ratio, via a hydrothermal process with 1-butyl-3-methylimidazolium hexafluorophosphate as carbon source in a $H_3PO_4$-ethanol medium.