# Fe<sup>3+</sup>-catalyzed low-temperature preparation of multicolor carbon polymer dots with capability for distinguishing D<sub>2</sub>O from H<sub>2</sub>O

Jie Xia, Yong-Liang Yu\* and Jian-Hua Wang\*

Research Center for Analytical Sciences, College of Sciences, Northeastern

University, Box 332, Shenyang 110819, China

#### **Corresponding authors.**

\*E-mail: yuyl@mail.neu.edu.cn (Y.-L. Yu); jianhuajrz@mail.neu.edu.cn (J.-H.

Wang)

Tel: +86 24 83688944; Fax: +86 24 83676698

## **Electronic Supplementary Information**

#### **Chemicals and materials**

*p*-Phenylenediamine (PPD), *o*-phenylenediamine (OPD), *m*-phenylenediamine (MPD) and FeCl<sub>3</sub>·6H<sub>2</sub>O were purchased from Aladdin Chemistry Co., Ltd. (Shanghai, China). Silica gel, ethyl acetate and ethanol were purchased from Sinopharm Chemical Reagent Co., Ltd. (China). Heavy water (D<sub>2</sub>O), methanol-d4 (MeOH-d4), dimethyl sulfoxide-d6 (DMSO-d6), acetonitrile-d3 (MeCN-d3) and acetone-d6 were purchased from Sigma-Aldrich Co., Ltd. (USA). All reagents were used as received without further purification. Ultrapure water (18 M $\Omega$  cm) was used throughout the experiments. 100 mM FeCl<sub>3</sub> aqueous solutions was prepared and stocked at 4 °C for further use. The Britton-Robinson (BR) buffer was prepared by mixing 40 mM acetic acid, boric acid, and phosphoric acid. pH value was adjusted by different amounts of 1 M NaOH or HCl solutions.

#### Instrumentations

Fluorescence (FL) spectra were recorded on an F-7000 spectrophotometer (Hitachi High-Technologies, Japan). Ultraviolet-visible (UV/Vis) absorption spectra were recorded on a U-3900 spectrophotometer (Hitachi High-Technologies, Japan). Transmission electron microscopy (TEM) observations were performed on a Tecnai  $G^{2}20$  transmission electron microscope (FEI, USA). Fourier transform infrared (FTIR) spectra were recorded on a Nicolet-6700 spectrophotometer (Thermo Instruments Inc., USA). X-ray photoelectron spectroscopy (XPS) scanning curves were obtained on an ESCALAB 250XI surface analysis system with Al/K $\alpha$  as the source (Thermo Electron, USA). Photoluminescence (PL) lifetime was measured using FluoroMax-4TCSPC spectrofluorometer (HORIBA Jobin Yvon, USA). PL quantum yields (QY) were measured on a FLS-1000 spectrophotometer (Edinburgh, England) based on an integrating sphere method.

#### **Preparation and purification**

Multicolor emissive CPDs were synthesized by using different molar ratios of PD to FeCl<sub>3</sub> in H<sub>2</sub>O at 80 °C. Typically, 10 mL of 10 mM PPD aqueous solution and 100 µL of 100 mM FeCl<sub>3</sub> aqueous solution were mixed with 89.9 mL of ultrapure water for synthesis of red emissive *p*-CPDs. The mixture was then transferred into sealed reaction containers of plastic or glass, heated to 80 °C, and kept for 24 h. The reaction solution was filtered with 0.22 µm membrane to remove the aggregates. The crude products were then purified by a silica column chromatography with ethyl acetate/ethanol mixture as eluent. The solid product was obtained by removing solvents and further drying under vacuum. By altering the precursor amounts and PD/FeCl<sub>3</sub> ratios, the CPDs with different emissive colors were synthesized. At the OPD concentration of 10 mM and the OPD/FeCl<sub>3</sub> ratio of 0.5, the yellow emissive o-CPDs were obtained through heating at 80 °C for 24 h; at the MPD concentration of 10 mM and the MPD/FeCl<sub>3</sub> ratio of 0.1, the blue emissive m-CPDs were obtained through heating at 80 °C for 48 h. The ratio of ethyl acetate and ethanol varies with the different CPDs. Generally, the ratio of ethyl acetate and ethanol is 4:1 for p-CPDs, 7:3 for o-CPDs and 3:2 for m-CPDs, respectively. For scalable preparation of the CPDs, the reaction volume can be either scaled up to 1 L or down to 10 mL, while all other reaction conditions were kept constant. In these cases, we supposed that the oxidative polymerization process and thermal aging effect may synergistically contribute to the formation of CPDs.

#### **General detection procedures**

Typically, for the H<sub>2</sub>O sensing experiments, 10 mg of *p*-CPDs powder was dispersed in 20 mL of D<sub>2</sub>O, followed by ultrasonication for 10 min to ensure the homogeneity of the suspension. Then 10  $\mu$ L of the prepared *p*-CPDs suspension was transferred to the quartz cells, followed by addition of different volumes of H<sub>2</sub>O. Subsequently, D<sub>2</sub>O was added to the quartz cells to keep the final volume of H<sub>2</sub>O/D<sub>2</sub>O mixture at 1 mL. Slight shaking was applied to these mixtures in the quartz cells to maintain uniform dispersion during the experiment. The fluorescence spectra were recorded using an excitation wavelength of 490 nm.



Fig. S1 PL emission intensity of (a) *p*-CPDs, (b) *o*-CPDs and (c) *m*-CPDs prepared under different reaction volumes ( $\lambda_{ex}/\lambda_{em} = 490/600$  nm for *p*-CPDs,  $\lambda_{ex}/\lambda_{em} = 400/550$ nm for *o*-CPDs,  $\lambda_{ex}/\lambda_{em} = 340/425$  nm for *m*-CPDs).



**Fig. S2** Histograms of particles size distribution of (a) *p*-CPDs, (b) *o*-CPDs and (c) *m*-CPDs corresponding to each TEM image.



**Fig. S3** UV/Vis absorption spectra of (a) PPD, (b) OPD and (c) MPD aqueous solutions.



**Fig. S4** UV-Vis absorption spectrum of Fe<sup>3+</sup> and PL excitation spectra of *p*-CPDs, *o*-CPDs and *m*-CPDs ( $\lambda_{em} = 600$  nm for *p*-CPDs,  $\lambda_{em} = 550$  nm for *o*-CPDs,  $\lambda_{em} = 425$  nm for *m*-CPDs).



**Fig. S5** PL emission intensity of (a) *p*-CPDs, (b) *o*-CPDs and (c) *m*-CPDs in BR buffered aqueous solutions with different pH values ( $\lambda_{ex}/\lambda_{em} = 490/600$  nm for *p*-CPDs,  $\lambda_{ex}/\lambda_{em} = 400/550$  nm for *o*-CPDs,  $\lambda_{ex}/\lambda_{em} = 340/425$  nm for *m*-CPDs).



**Fig. S6** PL emission intensity of (a) *p*-CPDs, (b) *o*-CPDs and (c) *m*-CPDs in salty solutions with different NaCl concentrations ( $\lambda_{ex}/\lambda_{em} = 490/600$  nm for *p*-CPDs,  $\lambda_{ex}/\lambda_{em} = 400/550$  nm for *o*-CPDs,  $\lambda_{ex}/\lambda_{em} = 340/425$  nm for *m*-CPDs).



**Fig. S7** PL emission intensity of (a) *p*-CPDs, (b) *o*-CPDs and (c) *m*-CPDs in oxidative solutions with different H<sub>2</sub>O<sub>2</sub> concentrations ( $\lambda_{ex}/\lambda_{em} = 490/600$  nm for *p*-CPDs,  $\lambda_{ex}/\lambda_{em} = 400/550$  nm for *o*-CPDs,  $\lambda_{ex}/\lambda_{em} = 340/425$  nm for *m*-CPDs).



Fig. S8 FTIR spectra of *p*-CPDs, *o*-CPDs, *m*-CPDs, and their corresponding raw

materials, i.e., PPD, OPD and MPD.



Fig. S9 XPS spectra of (a) *p*-CPDs, (b) *o*-CPDs and (c) *m*-CPDs.



**Fig. S10** Deconvoluted high-resolution C 1s (a-c), N 1s (d-f) and O 1s (g-i) XPS spectra of *p*-CPDs, *o*-CPDs and *m*-CPDs.



**Fig. S11** PL emission intensity of *p*-CPDs in D<sub>2</sub>O at  $\lambda_{ex}/\lambda_{em} = 490/600$  nm upon addition of 67 vol% H<sub>2</sub>O and BR buffered aqueous solutions with different pH values. (*p*-CPDs concentration: 5 µg mL<sup>-1</sup>)



**Fig. S12** PL spectral response of *p*-CPDs in D<sub>2</sub>O upon the addition of 67 vol% H<sub>2</sub>O and H<sub>2</sub>O containing various (a) metal ions, (b) organic species or (c) anions at 1 mM, and 0.5 mM for Al<sup>3+</sup> and Fe<sup>3+</sup>. (*p*-CPDs concentration: 5  $\mu$ g mL<sup>-1</sup>)



Fig. S13 (a) PL emission spectra and (b) normalized PL emission spectra of *p*-CPDs dispersed in different solvents at  $\lambda_{ex} = 490$  nm.

Ref.	Raw material	Driving force	Separation method	Formation mechanism	Application
1	Ascorbic acid (in water)	Cu <sup>2+</sup> , 90 °C	Null	Polymerization, nucleation	pH sensing
2	Saccharide (in water)	NaOH or NaHCO <sub>3</sub> ,	Dialysis	Decomposition, nucleation	Null
3	Sodium naphthalene, acetonitrile (in ethylene glycol dimethyl ether)	RT	Chromatography	Null	Bioimaging
4	Selenocystine (in water)	NaOH, 60 °C	Dialysis	Null	Free-radical scavenging
5	<i>p</i> -Benzoquinone, triethylenetetramine (in water)	RT	Chromatography	Schiff base condensation	Bioimaging
6	Cysteine (in water)	NaOH, 60 °C	Dialysis	Condensation, aggregation and carbonization	Affecting cellular energy metabolism
This work	Phenylenediamine (in water)	Fe <sup>3+</sup> , 80 °C	Chromatography	Oxidative polymerization, thermal aging effect	D <sub>2</sub> O/H <sub>2</sub> O sensing

### Table S1 Previous literatures concerning the formation of LT-CDs.

 Table S2 Some literatures concerning CDs with tunable PL emission through

regulation of N composition.

Ref.	Raw material	Synthetic method	Separation method	PL peak (nm)	PL mechanism
7	Phenylenediamine (in ethanol)	High pressure, 180 °C	Chromatography	423-604	Size effect, nitrogen content
8	Citric acid, urea (in formamide)	High pressure, 180 °C	Chromatography	460-630	Graphitic N content
9	L-Glutamic acid, <i>o</i> - phenylenediamine (in mixed solvents of formamide/dimethylformamide or ethanol/diluted sulfuric acid aqueous solution)	High pressure, 210 °C	Precipitation	443-745	Size effects, graphitic N content
10	Dihydroxybenzene, hydrazine hydrate (in water or ethanol)	High pressure, 180 °C	Dialysis	417-670	Size effect, nitrogen content and band gap
This work	Phenylenediamine (in water)	Fe <sup>3+</sup> , 80 °C	Chromatography	425-600	Graphitic N content

Sample	Concentration of $Fe^{3+}$ ( $\mu M$ )	$\lambda_{ex}$ (nm)	Φ (%)
<i>p</i> -CPDs	0	490	4.92±0.39
	100	490	4.88±0.29
	300	490	5.17±0.21
	500	490	4.81±0.52
o-CPDs	0	400	2.35±0.03
	100	400	2.32±0.02
	300	400	2.31±0.03
	500	400	2.29±0.02
<i>m</i> -CPDs	0	340	3.95±0.09
	50	340	3.88±0.14
	100	340	3.51±0.12
	300	340	3.25±0.19
	500	340	2.85±0.20

**Table S3** QY of the CPDs with different amounts of  $Fe^{3+}$ .

Sample	Absorption peak (cm <sup>-1</sup> )	Group	Vibration mode
	~3160-3400	N-H	stretching vibration
	1511, 1627	C=C	stretching vibration
PPD	1258	N-H	in-plane bending vibration
	1065, 1126	С-Н	in-plane bending vibration
	822	С-Н	out-of-plane bending vibration
	~3160-3400	N-H	stretching vibration
	1457-1630	C=C	stretching vibration
OPD	1247, 1271	N-H	in-plane bending vibration
	1030-1154	С-Н	in-plane bending vibration
	742	С-Н	out-of-plane bending vibration
	~3160-3400	N-H	stretching vibration
	1492, 1586	C=C	stretching vibration
MPD	1315	N-H	in-plane bending vibration
	1064-1194	С-Н	in-plane bending vibration
	775	С-Н	out-of-plane bending vibration
	~3400-3600	O-H	stretching vibration
	~3160-3400	N-H	stretching vibration
	~2820-2920	С-Н	stretching vibration
n CDDa	1640-1690	C=N/C=O	stretching vibration
p-CPDs	1517, 1632	C=C	stretching vibration
	1402	C-N=	stretching vibration
	1138	С-Н	in-plane bending vibration
	824	С-Н	out-of-plane bending vibration
	~3400-3600	О-Н	stretching vibration
	~3160-3400	N-H	stretching vibration
	~2820-2920	С-Н	stretching vibration
	1683	C=N/C=O	stretching vibration
0-CI D5	1529, 1632	C=C	stretching vibration
	1340-1400	C-N=	stretching vibration
	1148	С-Н	in-plane bending vibration
	751	С-Н	out-of-plane bending vibration
	~3400-3600	O-H	stretching vibration
	~3160-3400	N-H	stretching vibration
	2854	С-Н	stretching vibration
m CDDa	1640-1690	C=N/C=O	stretching vibration
m-CrD8	1561, 1621	C=C	stretching vibration
	1340-1400	C-N=	stretching vibration
	1159	С-Н	in-plane bending vibration
	781	С-Н	out-of-plane bending vibration

 Table S4 FTIR spectra analysis of the raw materials and the CPDs.

Binding energy (eV)	Chemical bond	<i>p</i> -CPDs	o-CPDs	<i>m</i> -CPDs
284.7	C-C/C=C	50.9	65.6	81.8
286.0	C-N/C-O	42.8	30.3	16.4
288.5	C=O/C=N	6.2	4.1	1.8
399.0	Amino N	50.4	64.3	69.6
400.0	Pyrrolic N	18.0	26.0	24.7
401.5	Graphitic N	31.7	9.7	5.6
532.2	С=О	54.2	54.3	54.3
533.2	C-0	45.8	45.7	45.7

**Table S5** High-resolution C1s, N1s and O1s XPS spectra analysis of the CPDs.

**Table S6** Comparison of the analytical characteristics of various materials forfluorescence sensing  $H_2O$  in  $D_2O$ .

Material	Mode	LOD (vol%)	Linear range (vol%)	Ref.
Nanocrystal	Turn on	0.0009	/	11
MOF	Ratiometric	0.001	0.001–12	12
Fluorophore	Ratiometric	0.080	0–47.1	13
LT-CD	Turn off	0.10	0.40–67	This work

#### References

- 1. X. F. Jia, J. Li and E. K. Wang, *Nanoscale*, 2012, 4, 5572-5575.
- Y. S. Li, X. X. Zhong, A. E. Rider, S. A. Furman and K. Ostrikov, *Green Chem.*, 2014, 16, 2566-2570.
- C. Yang, S. Zhu, Z. Li, Z. Li, C. Chen, L. Sun, W. Tang, R. Liu, Y. Sun and M. Yu, *Chem. Commun.*, 2016, **52**, 11912-11914.
- F. Li, T. Y. Li, C. X. Sun, J. H. Xia, Y. Jiao and H. P. Xu, *Angew. Chem., Int. Ed.*, 2017, 56, 9910-9914.
- M. L. Liu, L. Yang, R. S. Li, B. B. Chen, H. Liu and C. Z. Huang, *Green Chem.*, 2017, **19**, 3611-3617.
- F. Li, Y. Y. Li, X. Yang, X. X. Han, Y. Jiao, T. T. Wei, D. Y. Yang, H. P. Xu and G. J. Nie, *Angew. Chem., Int. Ed.*, 2018, 57, 2377-2382.
- K. Jiang, S. Sun, L. Zhang, Y. Lu, A. G. Wu, C. Z. Cai and H. W. Lin, *Angew. Chem., Int. Ed.*, 2015, **54**, 5360-5363.
- K. Hola, M. Sudolska, S. Kalytchuk, D. Nachtigallova, A. L. Rogach, M. Otyepka and R. Zboril, *ACS Nano*, 2017, **11**, 12402-12410.
- H. Ding, J. S. Wei, P. Zhang, Z. Y. Zhou, Q. Y. Gao and H. M. Xiong, *Small*, 2018, 14, 1800612.
- 10. Y. Y. Wang, Q. Su and X. M. Yang, Chem. Commun., 2018, 54, 11312-11315.
- 11. I. A. Mir, K. Rawat and H. B. Bohidar, Cryst. Res. Technol., 2016, 51, 561-568.
- S. G. Dunning, A. J. Nunez, M. D. Moore, A. Steiner, V. M. Lynch, J. L. Sessler,
   B. J. Holliday and S. M. Humphrey, *Chem*, 2017, 2, 579-589.

 Y. J. Luo, C. Li, W. C. Zhu, X. J. Zheng, Y. Huang and Z. Y. Lu, *Angew. Chem.*, *Int. Ed.*, 2019, **58**, 6280-6284.