## One-step synthesis of a dual-emitting carbon dot-based ratiometric fluorescent probe for visual assay of lead and PPi and paper sensor

Yifang Gao,<sup>a</sup> Yuan Jiao,<sup>a</sup> Huilin Zhang,<sup>a</sup> Wenjing Lu, <sup>a</sup> Yang Liu,<sup>a</sup> Hui Han, <sup>a</sup> Xiaojuan Gong,<sup>a</sup> Lei Li,<sup>a, b</sup> Shaomin Shuang<sup>a</sup> and Chuan Dong<sup>\*a</sup>

## Experimental

## Instrumentations

Transmission electron microscope (TEM) images were obtained on a JEOL JEM-2100 transmission electron microscope (Tokyo, Japan) at a voltage of 300 kV. Absorption spectra were collected using a Lambda 365 spectrophotometer (PerkinElmer, Llantrisant, U.K.). Fluorescence spectra and steady-state fluorescence were recorded on a Hitachi F-4500 fluorescence spectrophotometer. Absorption spectra were recorded using a Lambda 365 spectrophotometer (PerkinElmer, Llantrisant, U.K.). X-ray photoelectron spectroscopy (XPS) data was gotten using an AlK $\alpha$  radiation at 1486.6 eV on an AXIS ULTRA DLD X-ray photoelectron spectrometer (Kratos, Tokyo, Japan).Elemental analysis data were achieved by analysis of elemental analysis system element EL cube element analyzer (Hanau, Germany). Spectral plots were fitted to the peak fitting program via a symmetric symmetrical Gaussian-Lorentzian function through Case XPS v.2.3.12 software. A Fourier transform infrared (FTIR) spectra was tested on a Bruker Tensor IIFTIR spectrometer (Bremen, Germany). The time-resolved luminescence spectra were measured by means of the Edinburgh FLS920 fluorescence spectrophotometer. Images were accomplished through a confocal laser scanning microscope (LSM880+Airyscan, Zeiss).

## **Determination of QY**

The quantum yield  $\Phi$ s of the CDs were determined by a comparative method as follows:

 $\Phi_{\rm S} = \Phi_{\rm R}({\rm Grad}_{\rm S}/{\rm Grad}_{\rm R}) (\eta_{\rm S}^2/\eta_{\rm R}^2)$ 

where Grad is the gradient from the plot of integrated fluorescence intensity against absorbance and  $\eta$  (1.33) is the refractive index of the solvent. The subscripts S and R represent CDs and the reference (quinine sulfate in 0.10 M H<sub>2</sub>SO<sub>4</sub>). To prevent the re-absorption effect, the absorbances of CDs and quinine sulfate solutions in the 10-mm fluorescence cuvette were adjusted to less than 0.10 at the excitation wavelength ( $\lambda$ ex) of 380 nm (i.e., the absorption maximum of CDs). The integrated fluorescence intensity was the area under the PL curve in the wavelength range 400–700 nm. The  $\Phi$ R was taken as 0.54 since it is almost independent (within 5%) with  $\lambda$ ex at 200–400 nm.

 Table S1. Elemental analysis of the as-synthesised CDs.

Sample name	Elemental content (%)				
	С	Н	N	O (Calculated)	
CDs	30.7	6.2	15.2	47.9	

**Table S2**. Lifetime calculations from the time-resolved decay profiles of CDs, CDs-Pb<sup>2+</sup>and CDs-Pb<sup>2+</sup>-PPi.

Sample	τ1 (ns)	Percentage (%)	τ2 (ns)	Percentage (%)	Ave. $\tau$ (ns)
CDs	4.3242	87.77	11.5887	12.23	5.21
CDs-Pb <sup>2+</sup>	4.0247	82.16	9.3701	17.84	4.98
CDs-Pb <sup>2+</sup> -PPi	4.2956	89.31	12.5201	10.69	5.17

**Table S3.** Comparison of detection limit between the proposed fluorescent sensor andother reported detection methods for  $Pb^{2+}$ .

Sensing probe	Method	Response	Detection limits	Reference
		region		
B-C-dots	Fluorescence	25-250 μM	8.47 nM	1
CDs	Fluorescence	0.5 <b>-</b> 110 μM	0.5 μΜ	2
C-Dots	Fluorescence	0-12 mM	5.05 µM	3
Gold Nanoparticle	Colorimetric	0.1 <b>-</b> 2 μM	100 nM	4
Gold nanoparticles	Electrochemistry	0.30-1.40 μM	0.3 μM	5
[PAH <sup>b</sup> –GO <sup>c</sup> ] <sub>n</sub> /GCE	Electrochemistry	0.50-50 μM	0.35 μM	6
CDs	Ratiometric	0.18-510 μM	0.055 μM	This work
	fluorescent			

**Table S4.** Comparison of detection limit between the proposed fluorescent sensor and other reported detection methods for PPi.

Sensing probe	Method	Response	Detection	Reference
		region	limits	
N-doped CDs	Ratiometric	1-20 μM	0.7 µM	7
	fluorescent			
Nitrogen-doped CDs	Fluorescence	1-20µM	0.16 µM	8
CQDs/Ce(III)	Fluorescence	0.3-29.7 μM	0.1 µM	9
CDs	Fluorescence	0.5-80 μM	0.11 μΜ	10
Spiropyran	Fluorescence	1-500 μM	0.4 µM	11
CDs-Pb <sup>2+</sup>	Ratiometric	0.29-97.67 μM	0.089 µM	This work
	fluorescent			



Fig. S1 High-resolution XPS data of C 1s (A), N 1s (B) and O1s (C) of CDs.



Fig. S2 FL emission spectra of the CDs under different excitation wavelengths.



**Fig. S3** Effect of time intervals of irradiation with xenon arc light on fluorescence intensity of CDs.



Fig. S4 Effect of ionic strength on fluorescence intensity of CDs.



Fig. S5 The influence of different metal ions on the fluorescence of CDs.



Fig. S6 The influence of different different anion on the fluorescence of CDs-Pb<sup>2+</sup>.



Fig. S7 The FT-IR spectrum of the CDs, CDs-Pb<sup>2+</sup> and CDs-Pb<sup>2+</sup>-PPi.



Fig. S8 The UV-vis spectrum of the CDs, CDs-Pb<sup>2+</sup> and CDs-Pb<sup>2+</sup>-PPi.



**Fig. S9** The fluorescence emission decay curves of CDs, CDs-Pb<sup>2+</sup> and CDs-Pb<sup>2+</sup>-PPi in aqueous solution.



Fig. S9 Time-dependent of a CDs-Pb<sup>2+</sup> after introduction of PPi.

- Z.-X. Wang, X.-H. Yu, F. Li, F.-Y. Kong, W.-X. Lv, D.-H. Fan and W. Wang, *Microchimica Acta*, 2017, **184**, 4775-4783.
- Q. Wang, S. Zhang, H. Ge, G. Tian, N. Cao and Y. Li, *Sensors and Actuators B: Chemical*, 2015, 207, 25-33.
- 3. S. S. Wee, Y. H. Ng and S. M. Ng, *Talanta*, 2013, **116**, 71-76.
- 4. J. Liu and Y. Lu, Journal of the American Chemical Society, 2005, 127, 12677-12683.
- 5. X. Xu, G. Duan, Y. Li, G. Liu, J. Wang, H. Zhang, Z. Dai and W. Cai, ACS applied materials & interfaces, 2013, 6, 65-71.
- H. Liu, S. Li, D. Sun, Y. Chen, Y. Zhou and T. Lu, *Journal of Materials* Chemistry B, 2014, 2, 2212-2219.
- W. J. Zhang, S. G. Liu, L. Han, H. Q. Luo and N. B. Li, Sensors and Actuators B: Chemical, 2019, 283, 215-221.
- Y. Hu, X. Geng, L. Zhang, Z. Huang, J. Ge and Z. Li, *Scientific reports*, 2017, 7, 5849.
- 9. L. J. Chai, J. Zhou, H. Feng, J. J. Lin and Z. S. Qian, *Sensors and Actuators B: Chemical*, 2015, **220**, 138-145.
- H. Diao, T. Li, R. Zhang, Y. Kang, W. Liu, Y. Cui, S. Wei, N. Wang, L. Li and H. Wang, Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, 2018, 200, 226-234.
- N. Shao, H. Wang, X. Gao, R. Yang and W. Chan, *Analytical chemistry*, 2010, 82, 4628-4636.