Supporting information for

# One-step Solvothermal Synthesis of Dye-based Multicolor Fluorescent Carbon Dots for Information Encryption and Anti-counterfeiting Applications

*Yi Zhou*[a], *Hai-lin Duan*[a], *Ke-jun Tan*[*,a], *Lin Dong*[b]

[a]Key Laboratory of Luminescence Analysis and Molecular Sensing, Ministry of Education, College of Chemistry and Chemical Engineering, Southwest University, Chongqing 400715, P. R. China; E-mail: tankj@swu.edu.cn, Tel: +86-23-68367257, Fax: +86-23-68367257.

[b]School of the Environment, Jiangsu Key Laboratory of Vehicle Emissions Control, Center of Modern Analysis, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing, 210093, P. R. China.

## Experimental section

**Characterization techniques.** Fluorescence spectra were performed with the HITACHI F-2700 fluorescence spectrophotometer (Tokyo, Japan). Ultraviolet-visible absorption spectra were collected on a UV-2600 spectrophotometer (Shimadzu, Japan). The morphology, particle size and lattice of the CDs were characterized using a Talos F200X high resolution transmission electron microscope (TEM) (Thermo Fisher, USA). The fluorescence decay was obtained with an FLS980 steady-state/transient fluorescence spectrometer (Edinburgh, UK). The elemental composition and functional group class of the CDs were characterized by a Thermo Scientific Escalab 250Xi X-ray photoelectron spectrometer (Thermo Fisher, USA) and a Nicolet 5700 Fourier

Transform Infrared (FTIR) spectrometer (Nicolet, USA). XRD images were taken on a D8 ADVANCE X-ray diffractometer (Bruker, Germany).

**Quantum yield (QY) measurement.** The QYs of the three CDs were determined by the reference method at room temperature. Quinine sulfate (QY=54% in 0.01 M $H_2SO_4$) was selected as the reference for B-CDs and G-CDs, while Rhodamine B (QY=65% in ethanol) was chosen as the reference for R-CDs. The equation used is as follows[1]:

$$\Phi_X = \Phi_R \left(\frac{m_x}{m_R}\right)\left(\frac{\eta_x^2}{\eta_R^2}\right)$$

where $\Phi$ is the QY and $m$ represents the slope of the linear fit curve between the integral area of the fluorescence intensity and its corresponding absorption intensity.

η is the refractive index of the solvent (1.33 of water and 1.36 of ethanol). The subscripts"x"and "R"refer to the sample CDs and the standards, respectively. Absorbance values for both samples and standard solutions were kept below 0.1 to prevent the re-absorption effect.

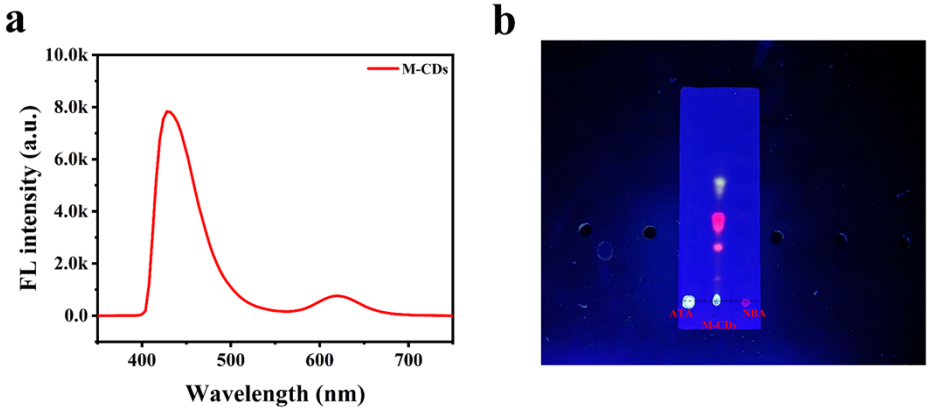


***Figure S1***. (a) Fluorescence emission spectra of M-CDs. (b) Thin-layer chromatography was performed on ATA, M-CDs and NBA respectively.

***Figure S2***. The images are photographs of reaction mixtures prepared at different reaction temperatures with ATA and NBA as co-reactants under daylight (top) and 365 nm UV light (bottom). From left to right, these samples were prepared at 120, 140, 160, 180 and 200 °C, respectively.

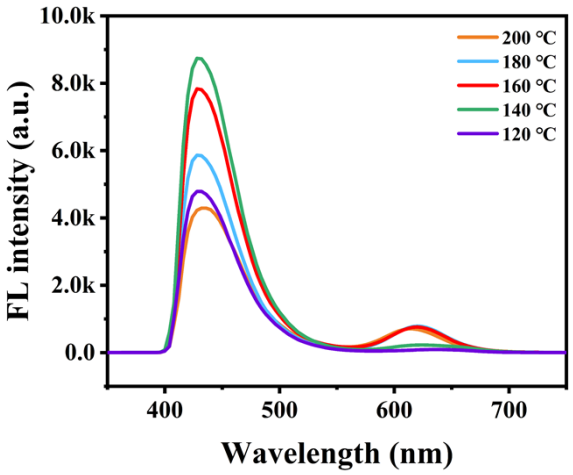


***Figure S3***. Fluorescence emission spectra of M-CDs at different reaction temperatures.

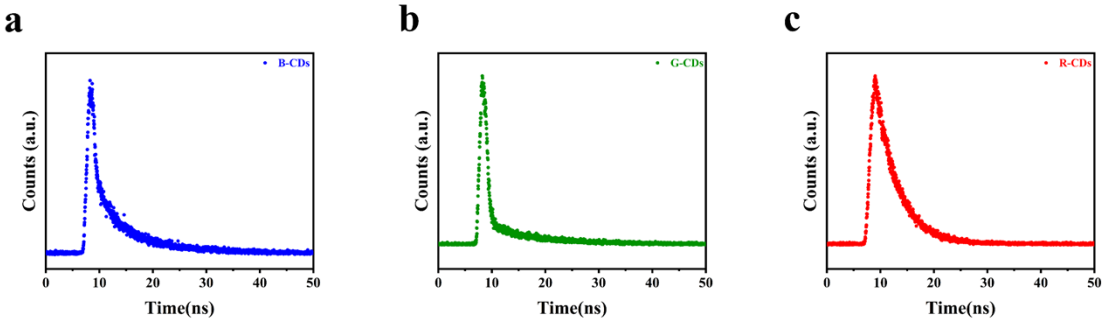


***Figure S4***. PL delay curves of (a) B-CDs, (b)G-CDs, and (c)R-CDs, respectively.

***Table S1.*** PL lifetimes of B-CDs, G-CDs and R-CDs in ethanol.

| Samples | $\tau_1$ (ns) | $B_1$(%) | $\tau_2$ (ns) | $B_2$(%) | $\tau_{avg}$(ns) | $\chi^2$ |
|---|---|---|---|---|---|---|
| B-CDs | 0.68 | 15.02 | 6.62 | 84.98 | 5.73 | 1.188 |
| G-CDs | 0.50 | 27.60 | 9.05 | 72.40 | 6.69 | 1.182 |
| R-CDs | 4.06 | 100.00 | \ | \ | 4.06 | 1.027 |

***Table S2.*** QYs data of B-CDs, G-CDs, and R-CDs references, respectively.

| Samples | Absorbance | Integrated Area | Slope | QYs (%) |
|---|---|---|---|---|
| Quinine Sulfate | 0.014 | 249109.154 | $1.6523\times10^7$ | 54.00 |
| | 0.016 | 269186.758 | | |
| | 0.023 | 398029.191 | | |
| | 0.037 | 642224.787 | | |
| | 0.041 | 676786.983 | | |
| Quinine Sulfate | 0.017 | 244313.582 | $1.5547\times10^7$ | 54.00 |
| | 0.022 | 318050.803 | | |
| | 0.030 | 392376.246 | | |
| | 0.034 | 453878.719 | | |
| | 0.043 | 548620.878 | | |
| Rhodamine B | 0.020 | 106087.806 | $4.5864\times10^6$ | 65.00 |
| | 0.026 | 142532.582 | | |
| | 0.036 | 189458.878 | | |
| | 0.045 | 227333.75 | | |
| | 0.056 | 273533.198 | | |

***Table S3.*** QYs data of B-CDs, G-CDs, and R-CDs.

| Samples | Absorbance | Integrated Area | Slope | QYs (%) |
|---|---|---|---|---|
| B-CDs | 0.024 | 172288.458 | $6.9478\times10^6$ | 22.71 |
| | 0.033 | 238137.762 | | |
| | 0.042 | 280398.606 | | |
| | 0.056 | 391008.043 | | |
| | 0.073 | 513397.547 | | |
| G-CDs | 0.026 | 54777.146 | $2.7606\times10^6$ | 9.59 |
| | 0.037 | 87013.286 | | |
| | 0.046 | 111147.38 | | |
| | 0.052 | 125509.485 | | |
| | 0.068 | 171743.043 | | |
| R-CDs | 0.023 | 33246.329 | $1.3246\times10^6$ | 18.77 |
| | 0.027 | 39548.344 | | |
| | 0.047 | 66130.155 | | |
| | 0.064 | 86958.755 | | |
| | 0.068 | 94130.978 | | |

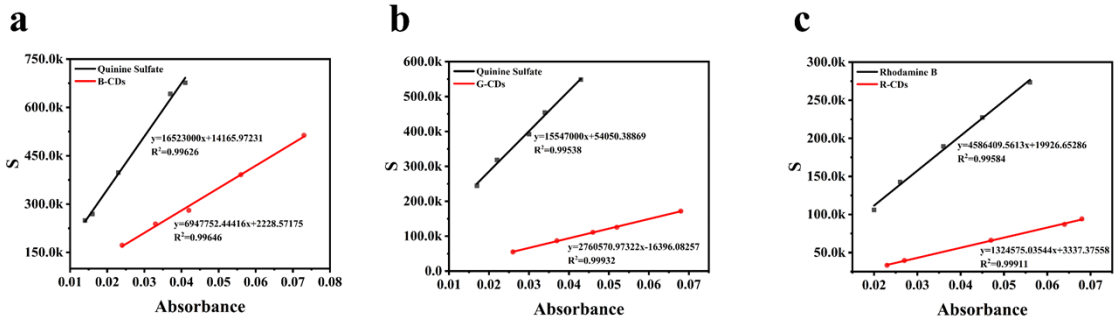


***Figure S5.*** Plots of integrated PL intensity against absorbance of (a) Quinine Sulfate, B-CDs, (b) Quinine Sulfate and G-CDs and (c) Rhodamine B and R-CDs, respectively.

***Table S4.*** Summary of representative multicolor CDs and CDs in this work.

| Raw materials | Reaction conditions | Emission wavelength | QYs | Reference |
|---|---|---|---|---|
| Citric acid and urea | 180 ℃, 12 h | 460-630 nm | 4.0%-13.1% | 2 |
| L-tyrosine and o-phenylenediamine | 180 ℃, 18 h | 451-590 nm | 8.6%-20.9% | 3 |
| Catechol m-dihydroxybenzene hydroquinone 1,6-dihydroxynaphthalene | 200 ℃, 2-7 h | 450-598 nm | 23.85%-50.54% | 4 |
| Melamine and Citric acid | 180 ℃, 8 h | 450-650 nm | 4.28%-4.95% | 5 |
| o-phenylenediamine and nickel chloride hexahydrate | 180 ℃, 1 h-20 h | 513-612 nm | 5.03%-11.82% | 6 |
| Citric acid | 200 ℃, 6 h | 470-595 nm | 21.9%-24.2% | 7 |
| 2,3-Diaminopyridine | 180 ℃, 6 h | 382-594 nm | 8.4%-9.3% | 8 |
| o-phenylenediamine with aniline, 1,8-diaminonaphthalene and [1,1′-binaphthalene]-2,2′-diamine | 180 ℃, 12 h | 440-580 nm | 11.0%-59.0% | 9 |
| o-phenylenediamine and m-aminophenol | 180 ℃, 12 h | 397-650 nm | 8.70%-23.66% | 10 |
| Tea polyphenol and o-phthalaldehyde | 200℃, 6 h | 443-585 nm | 21.0%-33.0% | 11 |
| 2-aminoterephthalic acid and Nile Blue A | 160 ℃, 8 h | 440-628 nm | 9.59%-22.71% | This work |

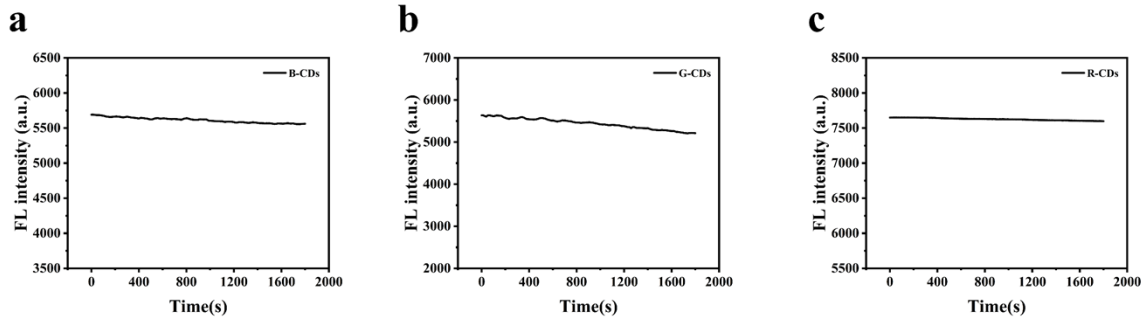


***Figure S6.*** Photobleaching Stability Tests for (a) B-CDs, (b)G-CDs, and (c)R-CDs, respectively.

***Table S5.*** Full width at half maxima (FWHM) values of the XRD diffraction peaks of B-CDs, G-CDs and R-CDs.

| Samples | FWHM |
|---|---|
| B-CDs | 5.4838 |
| G-CDs | 5.3942 |
| R-CDs | 5.3405 |

***Table S6.*** Carbon (C), oxygen (O) and nitrogen (N) elements of B-CDs, G-CDs and R-CDs.

| Samples | C (%) | O (%) | N (%) |
|---|---|---|---|
| B-CDs | 65.06 | 32.69 | 2.25 |
| G-CDs | 69.26 | 29.18 | 1.56 |
| R-CDs | 67.56 | 30.45 | 1.99 |

***Table S7*** The fitting results of the high resolution XPS spectra of C1s for B-CDs, G-CDs, and R-CDs.

| Samples | C-C/C=C (%) | C-N/C-O (%) | C=O/C=N (%) | O-C=O (%) |
|---|---|---|---|---|
| B-CDs | 64.92 | 17.66 | 8.39 | 9.03 |
| G-CDs | 66.83 | 25.42 | 3.84 | 3.91 |
| R-CDs | 69.59 | 21.28 | 6.10 | 3.03 |

***Table S8*** The fitting results of the high resolution XPS spectra of O1s for B-CDs, G-CDs, and R-CDs.

| Samples | C=O (%) | C-O (%) | O-C=O (%) |
|---|---|---|---|
| B-CDs | 27.24 | 50.30 | 22.45 |
| G-CDs | 6.73 | 78.19 | 15.08 |
| R-CDs | 22.48 | 62.14 | 15.38 |

***Table S9*** The fitting results of the high resolution XPS spectra of N1s for B-CDs, G-CDs, and R-CDs.

| Samples | Pyridinic N (%) | Amino N (%) |
|---|---|---|
| B-CDs | 32.83 | 67.17 |
| G-CDs | 35.71 | 64.29 |
| R-CDs | 29.87 | 70.13 |

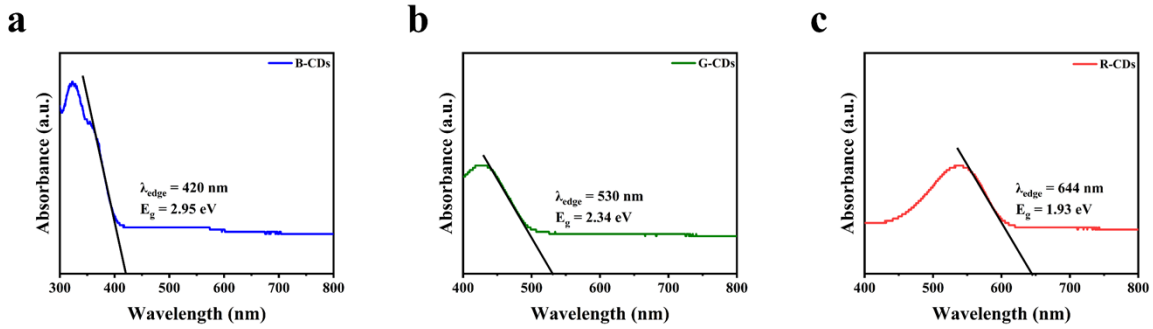


***Figure S7.*** Determination of the band gap energy ($E_g$) of (a) B-CDs, (b)G-CDs, and (c) R-CDs from UV-vis absorption spectrum.

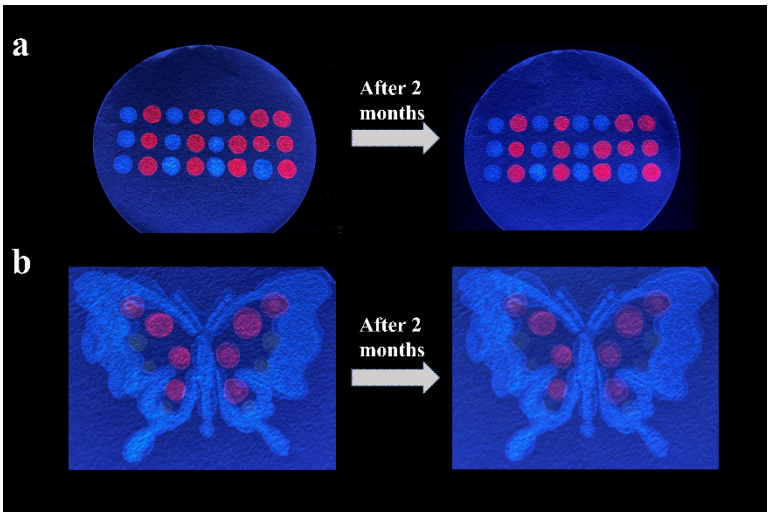


***Figure S8.*** Multi-color CDs ink after two months of sitting.

**Reference**


1. M. Moniruzzaman, B. Anantha Lakshmi, S. Kim and J. Kim, *Nanoscale*, 2020, **12**, 11947-11959.
2. K. Holá, M. Sudolská, S. Kalytchuk, D. Nachtigallová, A. L. Rogach, M. Otyepka and R. Zbořil, *ACS Nano*, 2017, **11**, 12402-12410.
3. L. Jin, L. Zhang, L. Yang, X. Wu, C. Zhang, K. Wei, L. He, X. Han, H. Qiao, A. M. Asiri, K. A. Alamry and K. Zhang, *Journal of Materials Science & Technology*, 2020, **50**, 184-191.
4. F. Yan, H. Zhang, N. Yu, Z. Sun and L. Chen, *Sensors and Actuators B:*

*Chemical*, 2021, **329**, 129263.
5. G. Liu, D. Kong, J. Han, R. Zhou, Y. Gao, Z. Wu, L. Zhao, C. Wang, L. Wang and G. Lu, *Sensors and Actuators B: Chemical*, 2021, **342**, 129963.
6. Y. Wu, J. Li, X. Zhao and X. Gong, *Carbon*, 2023, **201**, 796-804.
7. X. Huo, H. Shen, R. Liu and J. Shao, *ACS Omega*, 2021, **6**, 26499-26508.
8. R. Dai, X. Chen, N. Ouyang and Y. Hu, *Chemical Engineering Journal*, 2022, **431**, 134172.
9. Z. Liu, X. Lu, M. Liu and W. Wang, *Journal*, 2023, **28**.
10. H. Hu, J. Li and X. Gong, *Applied Materials Today*, 2024, **37**, 102154.
11. M. Chen, C. Liu, H. Sun, F. Yang, D. Hou, Y. Zheng, R. Shi, X. He and X. Lin, *ACS Applied Materials & Interfaces*, 2024, **16**, 9182-9189.